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A THEORY OF BIOGENESIS OF LICHEN DEPSIDES AND DEPSIDONES

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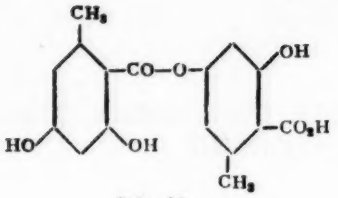
Received June 8, 1944

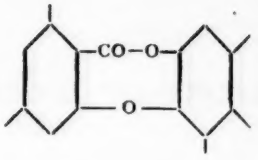
Lichens as a group are interesting not only botanically but also chemically. They are large in number and occur almost all over the globe. They have been used as food and also for the preparation of colouring matters, drugs and perfumes. In several respects their chemistry is unique. As reserve carbohydrates they possess lichenin and isolichenin instead of starch, and they frequently contain considerable amounts of sugar alcohols such as erythritol and mannitol. But their most characteristic components are the lichen acids which seem to be built on an altogether original pattern.

The first attempt at a classification of lichen components was made by Zopf in his book on lichens published in 1910. As the result of the large volume of later work which led to a clearer understanding of their chemistry, Zopf's scheme became obsolete and a better classification was given by Asahina[1] in 1934. He places them into three main classes: (A) compounds of the aliphatic and alicyclic series, (B) compounds of the aromatic series, and (C) substances of unknown nature. In each of the first two there are several groups and subgroups. Depsides form group IV and Depsidones group V under (B). They have the primary skeletons (I) and (II) respectively; the former corresponds to phenyl-benzoate and the latter has an oxygen bridge in addition. Each group has again been divided into two sub-groups, (1) Orcinol derivatives having nucleus (III) and (2) β-orcinol derivatives having nucleus (IV). A large number of these compounds are known and the constitutions of most of them are definitely established. When all the available data are carefully examined certain features come out strikingly and it seems to be possible to develop a general theory of biogenesis which may be useful for further work.

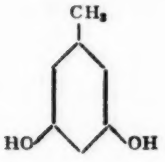
Though depsides and depsidones have been divided by Asahina into four groups for purposes of classification, structurally they are closely related and biogenetically they all seem to belong to one group. In the lichens, depsides and depsidones, orcinol and β-orcinol derivatives all occur together



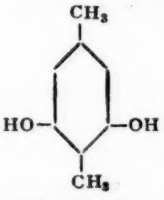
I depside



II depsidone



III Orcinol



IV β-Orcinol

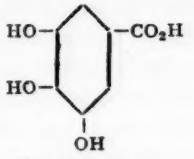
as the select examples given below (Table I) will show. It seems to be therefore definite that they are evolved from the same primary compound, the variations being brought about by processes of oxidation and reduction, and other simple reactions.

TABLE I

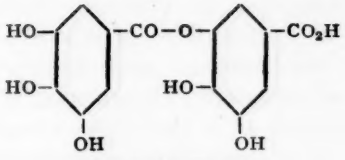
Parmelia abessinica	..	lecanoric acid (*a*), atranorin (*b*), salazinic acid (*d*).
P. Physodes and *furfuracea*	..	atranorin (*b*), physodic acid (*c*).
Evernia prunastri	..	evernic acid (*a*), atranorin (*b*).
Cetraria collata	..	atranorin (*b*), α-collatolic acid (*c*).
Lobaria pulmoria	..	gyrophoric acid (*a*), stictinic acid (*d*).
Usnea species	..	atranorin (*b*), protocetraric acid (*d*).
(*a*) = orcinol depside,		(*b*) = β-orcinol depside,
(*c*) = orcinol depsidone,		(*d*) = β-orcinol depsidone.

Comparison of lichen and tannin derivatives.—In recounting the characteristic features of the lichen acids, it may be useful to compare them with tannin derivatives. The latter are based on gallic acid (V *a*) and consist of meta-digallic acid units (V *b*). Frequently these are in combination with glucose or some other sugar. Lichen depsides (VI *b*) on the other hand are based on orsellinic acid (VI *a*) (including substituted or derived orsellinic acid) units. Occasionally they are found in combination with the sugar alcohol, erythritol as esters. Though they are mostly didepsides, some tridepsides are known such as gyrophoric acid, tenuiorin and umbilicaric acid. The majority of them are para-depsides and it seems to be due to the fact that in orsellinic acid no meta-hydroxyl is present. However if conditions should be favourable and if a meta-hydroxyl is made available by nuclear oxidation, meta-depsides result. Sekikaic acid, ramalinolic acid

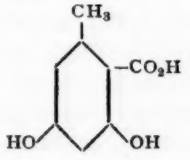
(XXXI), thamnolic and hypothamnolic[2] acids (XXXII) belong to this group of meta-depsides though some of them were earlier considered to be para-depsides. In view of the large occurrence of *m*-depsides in tannins and of Fischer's findings that acyl groups migrate readily from a para to a meta oxygen atom in gallic acid derivatives, meta-depsides should be more stable and may be expected to be found in the lichens also whenever meta-hydroxyls are present.



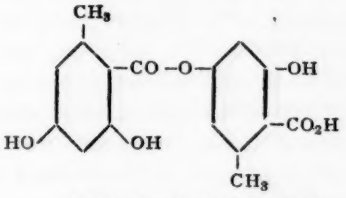
V*a* gallic acid



V*b* meta-digallic acid

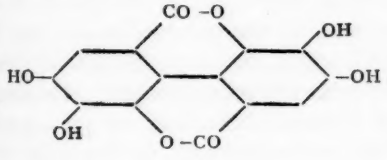


VI*a* Orsellinic acid



VI*b* Lecanoric acid (*p*-depside)

There is one other item of comparison and contrast between the tannin and lichen components. Ellagic acid (VII) could be compared with the lichen depsidones (VIII). Both seem to arise from nuclear oxidation or dehydrogenation of the corresponding depsides. The former is a diphenyl derivative whereas the latter has a diphenyl ether group. This difference is again due to structural restrictions since in orsellinic acid no free ortho-position is available and an ortho-hydroxyl has to be used for linking the two phenyl nucleii.



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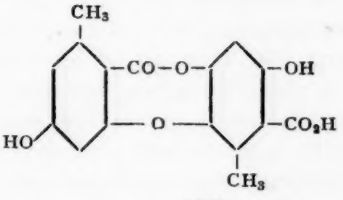


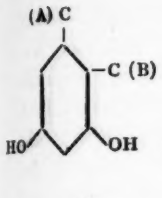
VIII

Occurrence of orsellinic acid unit (C_8 *unit*).—Though gallic acid which is the unit of tannin depsides occurs free in nature there was for a long time no definite proof of the occurrence of free orsellinic acid or its simple derivatives.

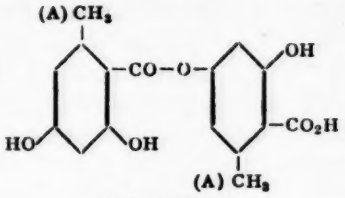
When esters of these acids were isolated in certain cases their presence was attributed to alcoholysis[3] taking place during the course of extraction. The discovery of montagnetol (*d*- as well as *dl*-) in the Indian lichen, *Roccella montagnei* by Rao and Seshadri[4] may therefore be said to be the first definite case of the existence of the single orsellinic acid unit. It is the erythrityl ester of orsellinic acid and has been obtained by methods of extraction which cannot involve any change in the nature of the components. Till recently there was the possibility that erythrin also might belong to this category; it interested us on this account. In Zerner's formula for this substance two orsellinic acid units are independently linked with one molecule of erythritol. The question of its constitution was raised in one of our publications in 1940[4a] and we announced that work was already in progress. It has now been independently investigated by Sakurai[5] and by Rao and Seshadri[6] who have shown definitely that it is the erythrityl ester of lecanoric acid. The work of the latter authors on this subject was complete in June 1941 and the paper was communicated for publication in April 1942. Due to the difficult conditions of war, particularly about that time, information about Sakurai's work reached us through the medium of the *British Chemical Abstracts* only after our paper had been published. Though the two investigations were planned somewhat differently the results common to both agree closely.

Free orsellinic acid has not so far been found in lichens ; orcinol is however present along with lecanoric acid in *Roccella tinctoria.* It definitely accompanies montagnetol in *Roccella montagnei.* The explanation of these observations already offered by us[7] seems to be satisfactory. Orsellinic acid is too unstable to remain free. It has to be stabilised by depside formation or by esterification with erythritol; otherwise it undergoes decarboxylation to yield orcinol.

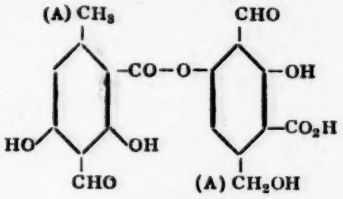
The foregoing discussion and a careful review of the structures of all known lichen depsides and depsidones lead to the conclusion that the C_8 skeleton (IX) characteristic of orsellinic acid is the basis for all of them. This is unique for lichens and does not seem to occur elsewhere. Orsellinic acid itself cannot be the fundamental substance, because though carbon atom (B) in the C_8 unit is always present as a carboxyl, carbon atom (A) is in different states of oxidation in a large number of the lichen acids and can be either CH_3, CH_2OH, CHO or CO_2H. Typical examples taken from different groups of lichen compounds are given below. In the structures of the molecules though there are other features, the orsellinic acid units alone should be considered; carbon atom (A) is marked.



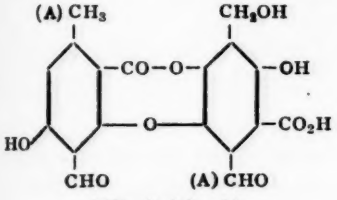
IX



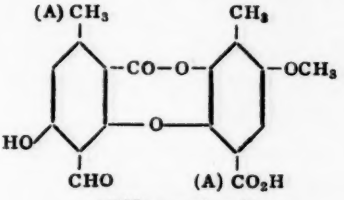
X lecanoric acid



XI barbatolic acid

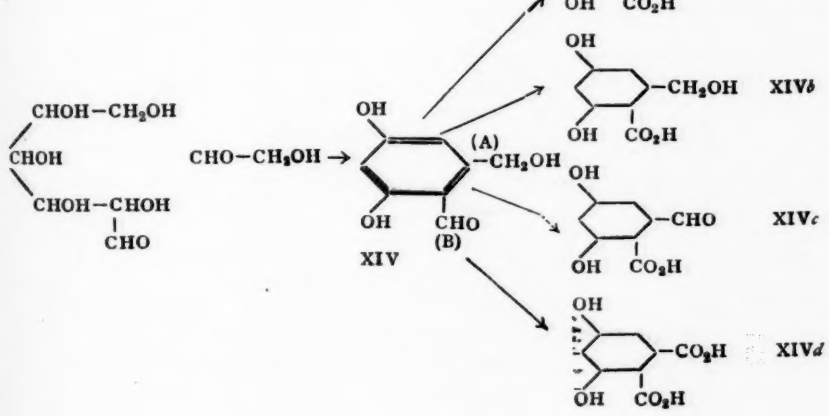


XII salazinic acid



XIII psoromic acid

Origin of the C_8 unit.—It is now suggested that as the first stage in phytochemical synthesis a reactive substance of the C_8 type (XIV) is produced from a molecule of hexose and one of biose by condensation of the aldol type and elimination of water, and modifications arise subsequently due to oxidation and reduction leading to the existing variations. Out of the four modifications, the first one (XIV *a*) is the most important and it seems to involve internal oxidation and reduction (internal oxygen adjustment). The possibility of XIV *b* or *c* giving rise to the others also exists.

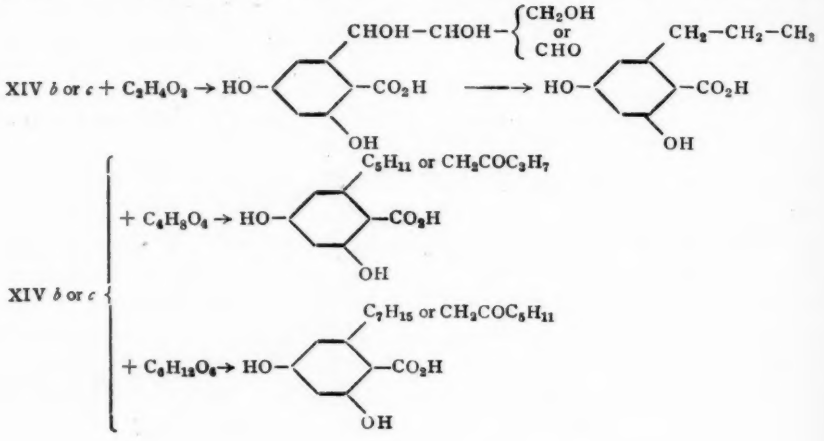


Evolution of longer side-chains.—In several lichen acids longer chains having odd number carbon atoms (3, 5 and 7) occur in the same place as (A). The interesting points to be noted in this connection are, (1) different chain lengths are found frequently in the same depside molecule and (2) in lichen thalli, compounds with one carbon atom in position (A) occur side by side with others having 3, 5 or 7-carbon-atom chains instead. It seems to be therefore reasonable to consider that the longer chains are the result of subsequent building up from the C_8 skeleton. In support of this idea it may be mentioned that frequently the second carbon atom in the chain and exceptionally the first are involved in a carbonyl group and this feature may be taken as an indication of the junction of two parts. Typical cases are given below:

(*a*) Lichen acids having different side-chains in the two halves: sphærophorin (CH_3 and C_7H_{15}), ramalinolic acid (C_3H_7 and C_5H_{11}), olivetoric and physodic acids (CH_2-CO-C_5H_{11} and C_5H_{11}), glomelliferic acid (CH_2-CO-C_3H_7 and C_5H_{11}), lobaric acid (CO-C_4H_9 and C_5H_{11}).

(*b*) Association of lichen acids with different chain lengths in the same lichen: Obtusatic acid (C_1) and sekikaic acid (C_3) occur together in Manchurian Ramalina. Atranorin (C_1) accompanies olivetoric acid (C_7 and C_5) in *Evernia furfuracea*, α-collatolic acid (C_7) in *Cetraria collata* and *Lecanora altra*, and divaricatic acid (C_3) in *Anzia japonica*. Salazinic acid (C_1) occurs together with lobaric acid (C_5) in Lobaria.

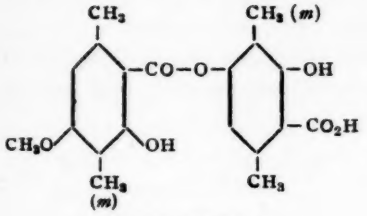
From the above data it may be concluded that derivatives of divarin (C_3), olivetol (C_5) and sphæropherol (C_7) are obtained from (XIV) or more probably from (XIV*b*) or (XIV*c*) by aldol condensation with biose, tetrose



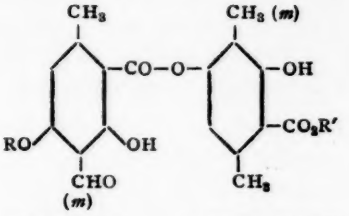
and hexose respectively and subsequent reduction. There is no direct support for the occurrence of biose in the lichens, but the availability of tetrose and hexose is indicated by the occurrence of erythritol, and of mannitol, lichenin and isolichenin. In the following discussion the term 'C_6 unit' includes these derivatives with longer chain lengths also.

Depsides: (i) *Orcinol derivatives.*—Depsides which are orcinol derivatives can be obtained by the combination of any two of the units XIV (*a*), (*b*), (*c*) and (*d*). Variations can again arise in the length of the side-chain methylation of the hydroxyl groups and esterification of the carboxyls. A very large number of possibilities therefore exist though many of them have not yet been found in nature. Whether all the above modifications take place prior to depside formation or after it, is not possible to say and may not be quite necessary for the present discussion.

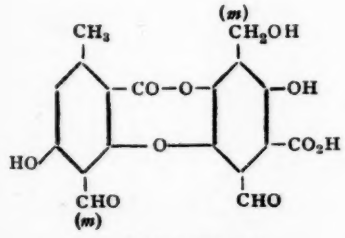
β-Orcinol derivatives: *nuclear methylation.*—Depsides which are β-orcinol derivatives are characterised by the presence of a susbtituent in the nuclear position between the two phenolic hydroxyl groups of the orsellinic acid unit. The substituent is not always a methyl group; it is frequently a carbinol, an aldehyde and even a carboxyl group. The following examples taken from both depsides and depsidones illustrate the point. The concerned nuclear position which is meta to the carboxyl is marked (*m*).



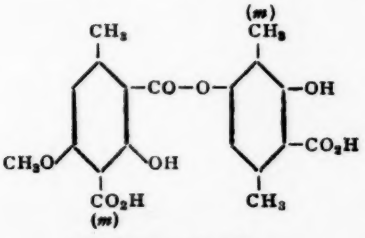
XV Barbatinic acid



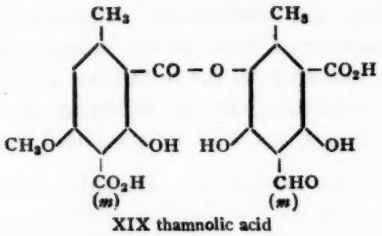
XVI Atranorin : R=H, R′=CH_3.
Beomycessic acid : R=CH_3, R′=H



XVII Salazinic acid

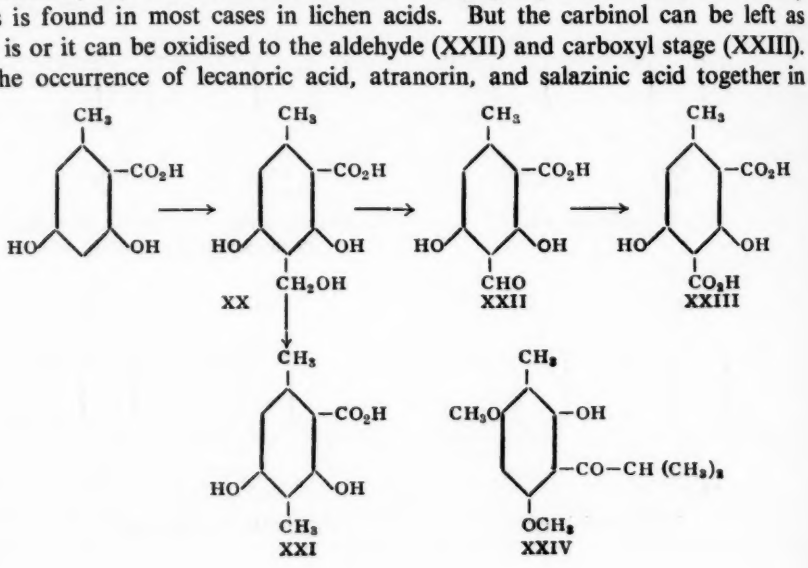


XVIII Squamatic acid



XIX thamnolic acid

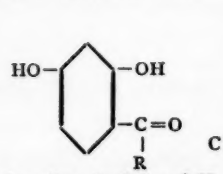
The position involved in the substitution is exactly where nuclear methylation in orsellinic acid and esters takes place in the laboratory and hence the formation of β-orcinol derivatives in lichens may be attributed to a similar process. The role of formaldehyde as a methylating agent for hydroxyl and amino groups is well known. The reaction involves the removal of oxygen as an essential stage. This may be effected by intramolecular adjustment as in the biogenesis of alkaloids[8] and also by means of some other reducing substances present in the system. In the laboratory the reagent itself serves this purpose and part of it undergoes oxidation. The reasonable assumption is made here that nuclear methylation is also brought about in the plant by means of formaldehyde. This explains very satisfactorily the existence of various stages of oxidation in the new side-chain. The primary product of the condensation of formaldehyde will be the carbinol (XX). If it suffers reduction a methyl group will be produced (XXI) as is found in most cases in lichen acids. But the carbinol can be left as it is or it can be oxidised to the aldehyde (XXII) and carboxyl stage (XXIII). The occurrence of lecanoric acid, atranorin, and salazinic acid together in



XX XXII XXIII XXI XXIV

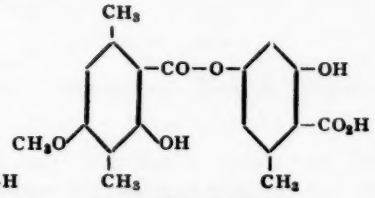
Parmelia abessinica and of beomycessic acid (XVI) and squamatic acid (XVIII) in ***Thamnolia vermicularia*** provide data in support of the above contention. A close laboratory analogy to this type of reaction is nuclear formylation using hexamine leading to the formation of aromatic hydroxy aldehydes.[9] The term 'nuclear methylation' is employed in the sequel in a general sense for the entry of the new side-chain and includes all the possible stages of oxidation given above. Nuclear methylation so facile in lichen acids, is not common elsewhere in natural products, but appears to take place occasionally when the conditions are favourable. Bæckeol[10] (XXIV) may be considered to be an example of a compound resulting from facile nuclear methylation.

The mechanism of nuclear methylation of phenolic-carbonyl compounds of the type (XXV) has been discussed in one of the past publications[11] from this laboratory. Crabtree and Robinson[12] have shown that a free hydroxyl in the 4th position is necessary for the reaction. It may therefore be concluded that in lichen acids nuclear methylation should precede depside formation, at least as far as the right half is concerned. Almost all β-orcinol derivatives have nuclear methylation in both the C_8 units involved. There is however a case of mixed depside in obtusatic acid (XXVI) and this lacks nuclear methylation in the right half. It is probably an instance where the reaction did not take place before depside formation and the left half got methylated after the depside stage. The occurrence of obtusatic acid along with evernic acid which is free from nuclear methylation in the two halves, in certain Ramalina species may be significant in this connection. But in general nuclear methylation may be said to precede depside formation. An important feature, which is in accordance with the above idea, is that in the lichens nuclear methylation is not necessarily accompanied by methylation of the neighbouring *p*-hydroxyl group and does not therefore interfere with subsequent depside formation.



R = alkyl, O-alkyl or O-H

XXV

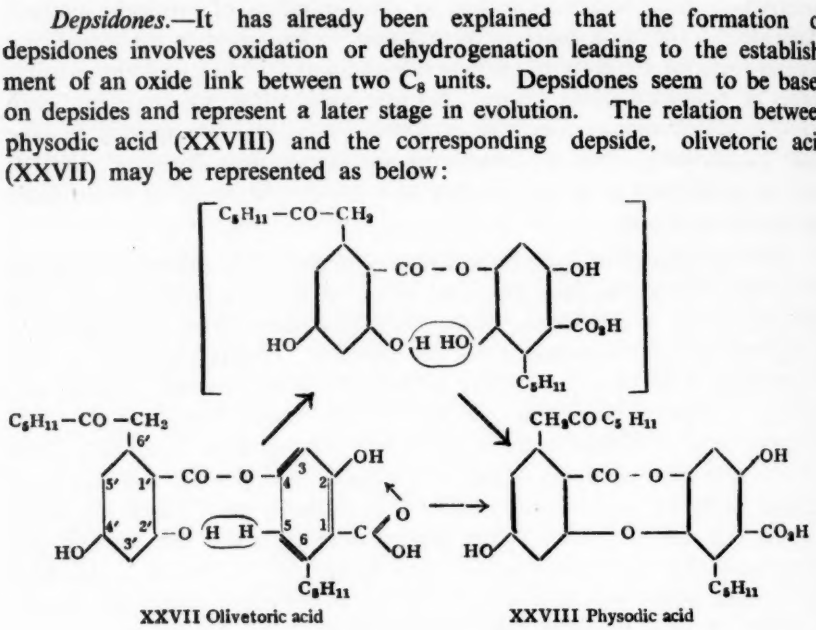


XXVI obtusatic acid.

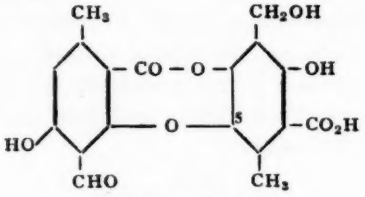
At this stage the large scope for the existence of different β-orcinol depsides may be considered. The β-orcinol halves can have variations in the original side-chain (A) of the C_8 unit and also in that arising from nuclear

methylation. Several combinations of these units can be chosen for depside formation. Further, methylation of the hydroxyl groups and esterification of carboxyls add to the possibilities.

Depsidones.—It has already been explained that the formation of depsidones involves oxidation or dehydrogenation leading to the establishment of an oxide link between two C_8 units. Depsidones seem to be based on depsides and represent a later stage in evolution. The relation between physodic acid (XXVIII) and the corresponding depside, olivetoric acid (XXVII) may be represented as below:



XXVII Olivetoric acid XXVIII Physodic acid



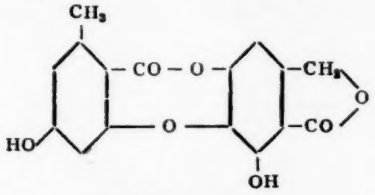
XXIX Protocetraric acid

The depside microphyllenic acid corresponds similarly to the depsidone α-collatolic acid.

In support of the above conclusion the following characteristics may be mentioned. In the left half of the molecule the ortho-hydroxyl (2′-position) has always to be used, but in the right half there are two alternative nuclear positions, 3 and 5, available for this purpose. Depsidone formation, however, seems to involve invariably position 5. This may be inevitable in β-orcinol derivatives (*e.g.*, proto-cetraric acid XXIX) since

nuclear methylation taking place earlier should have already used up position 3. The use of the 5th position even in orcinol derivatives indicates definitely that the reactions leading to depsidone link take place only after the depside stage, because the conditions for the preferential activation of the 3-position will not now exist. The hydroxyl in position 2 is now the activating group and the 5th position which is para to it, is activated more easily for purposes of oxidation or dehydrogenation. The possible fixation or preferential orientation of aromatic double bonds due to the existence of chelation[13] may also contribute to the lack of activity of position 3 and the comparatively greater reactivity of position 5 (see formula XXVII).

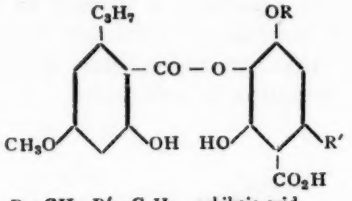
Quite recently Murphy, Keane and Nolan[14] have attributed to variolaric acid isolated from *Lecanora parella* the formula XXX. It is an orcinol derivative and the structure suggests that the 3-position is involved in the depsidone link. It seems to be therefore exceptional. However, it may be necessary to wait for a confirmation of this constitution before a variation in the above scheme of depsidone formation is recognised.



XXX Variolaric acid

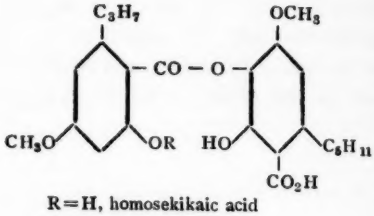
Meta-depsides.—Nuclear oxidation without leading to depsidone formation is also found in lichen acids. In most of these cases meta-depsides result. Sekikaic and Ramalinolic acids (XXXI) are two orcinol depsides in which the 3-position has undergone oxidation. They are closely related and are found to occur together in Ramalina species. Homosekikaic and boninic acids (XXXI *a*) are a similarly related pair. On the other hand, thamnolic and hypothamnolic acids (XXXII) are related β-orcinol depsides in which oxidation of position 5 is involved. With regard to their biogenesis it is significant that these *m*-depsides are associated with *p*-depsides in lichen thalli. Obtusatic (XXVI) and sekikaic (XXXI) acids occur together in Manchurian Ramalina; squamatic (XVIII) and thamnolic (XXXII) acids are found together in *Thamnolia varmicularis.* Thus there is indication that the two types have similar origin. It seems to be correct to consider that nuclear oxidation of the 3- or the 5-position takes place in the C_8 unit concerned prior to depside formation and since a meta-hydroxyl group is thus rendered available, a meta-depside results. The reactive position

will be the 3- in orcinol units and the 5- in β-orcinol units. The other alternative (*i.e.*) oxidation at the ordinary *p*-depside stage does not seem to be satisfactory and is not applicable to all cases as explained below. In the *p*-depsides the 3-position becomes unreactive and hence the formation of sekikaic, ramalinolic and related acids (XXXI) cannot be explained. Though the oxidation of the 5th position can take place after the depside stage, isomeric change to meta-depsides should then be assumed to occur subsequently under the conditions of the plant, and at the same time normal depsidone formation should be inhibited. The view that all the meta-depsides are due to oxidation taking place prior to depside formation is free from these defects and may therefore be accepted until new data render a change necessary.



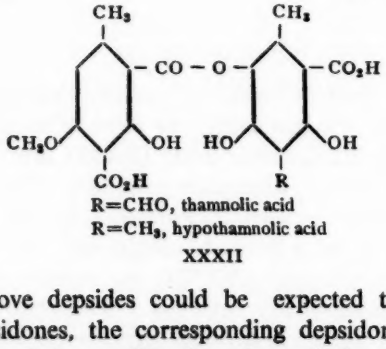
$R=CH_3$, $R'=C_3H_7$, sekikaic acid
$R=H$, $R'=C_5H_{11}$, ramalinolic acid

XXXI



$R=H$, homosekikaic acid
$R=CH_3$ boninic acid

XXXI*a*



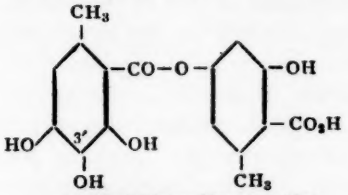
$R=CHO$, thamnolic acid
$R=CH_3$, hypothamnolic acid

XXXII

Though the above depsides could be expected to undergo dehydration and form depsidones, the corresponding depsidones do not seem to have been recorded. It is possible that they will be discovered in future, or there may be special reasons for the stability of these meta-depside molecules. Future work may throw light on this subject.

In the examples given above (depsidones as well as *m*-depsides) nuclear oxidation involves only the right half of the molecules concerned. There is one case where the left half is affected. It is diploschistesic acid[15] isolated from *Diploschistes scruposus* and having the constitution XXXIII. In

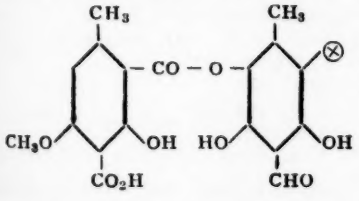
it nuclear position 3′ which is the most reactive in the left half, has undergone oxidation, possibly even after depside formation.



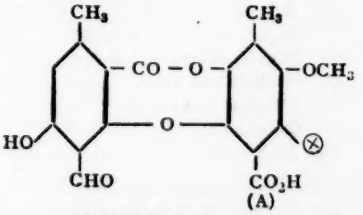
XXXIII Diploschistesic acid

In lichen acids the occurrence of methylation of the hydroxyl groups situated ortho to carboxyl groups is not unusual. Even in the laboratory these groups of the lichen depsides and depsidones undergo methylation under comparatively mild conditions using diazomethane or methyl iodide and potassium carbonate. This facility of methylation may be attributed to the weakening of the chelation existing between the concerned carbonyl and hydroxyl groups, the weakening being caused by the existence of substituents in positions ortho to these groups.[16]

To some extent decarboxylation of the lichen acids seems to take place in the plant. Decarboxylation is known to occur in the course of preparation on a large scale, particularly when the sample is boiled for a long time with solvents. The occurrence of decarboxy-thamnolic acid[2] (XXXIV) in commercial samples of thamnolic acid is attributed to this cause. The probable formation of orcinol from orsellinic acid has already been mentioned. A similar example belonging to the depsidone group seems to be psoromic acid[17] (XXXV) in which the original carboxyl (B) of the right half is lost; the one that remains seems to represent (A). The positions of the lost carboxyls are marked in the formulæ given below:



XXXIV Decarboxy thamnolic acid



XXXV Psoromic acid

Summary

Lichen depsides and depsidones are considered to arise from a common source (XIV) which originates from aldol condensation between a hexose and a biose and elimination of water. Oxidation and reduction lead to

various modifications of this C_8 unit and increase in the length of the side-chain arises from condensation with simple sugars and reduction. Depsides are formed by the combination of two of these units. β-Orcinol derivatives are obtained by nuclear methylation by means of formaldehyde and this reaction in general takes place prior to depside formation though the other possibility is not altogether excluded as far as the left half is concerned Depsidones come last in the evolution; they are based on depsides and require oxidation or dehydrogenation involving position 5 which is para to the activating hydroxyl. Nuclear oxidation without leading to depsidone formation also occurs. Either the 3- or the 5-position is involved and meta depsides result. Oxidation involving the left half is also possible and is represented by diploschistesic acid. The occurrence of orcinol and psoromic acid is attributed to decarboxylation taking place in the plant.

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Note.*—Formaldehyde has been shown by Hanus (*B. C. Abs.* AII, 1944, 14) to be capable of introducing carbinol (CH_2OH) groups into the nucleus of ortho-cresol in an alkaline medium. It has also been used for building this group on a ternary carbon atom in the course of the synthesis of Pantothenic acid (Stiller *et al.*, *J. A. C. S.*, 1940, 1785) and such a reaction has been considered to take place in the biogenesis of the above acid by Kuhn and Wieland (*B. C. Abs.* A II, 1942, 249). The method of nuclear methylation of phenolic substances using formaldehyde in the presence of a mineral acid described by Burawors (*Nature*, 1943, **151, 615) is rather complex in its mechanism.

THE MAGNETIC BEHAVIOUR OF A TEKTITE

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(From the Department of Physics, Indian Institute of Science, Bangalore)

Received June 14, 1944

(Communicated by Sir C. V. Raman, Kt., F.R.S., N.L.)

1. Introduction

This paper reports the results of a magnetic study of a specimen sent to Sir C. V. Raman for examination by Baron R. J. de Touche, being one amongst the several small black stones which were obtained by him in 1939 from the Manager of the Dutch Mining Company at the island of Billiton, when he visited the place on behalf of the Raffles Museum to examine a supposed find of meteorites. As a result of his investigations of the ancient literature, notably the records of the seventh century A.D., the Baron has identified these stones with the " magic stones " or " fire pearls " which were esteemed highly by the ancients and believed to have mystical powers. In his paper entitled " Discovery of the ancient magic stone of the Orient " (1944) to the Royal Asiatic Society, they are described as having a dark and sculptured surface suggestive of moon craters and appearing dark green at the edges which were thin. The material was found to be extremely hard and it is reported that " during the cutting and polishing process of one specimen, the surface of the polishing steel disc was so severely cut that it became pitted with deep holes ". The specimen sent for examination had a part of its surface cut and polished plane, while the rest of it had the original ovoid form of the stone and was marked with deep grooves.

2. Experimental Data

The specimen was tested for magnetic anisotropy by suspending it in a uniform magnetic field by a calibrated quartz fibre. The tendency to take up a definite equilibrium position was very feeble and this feeble anisotropy was determined for three mutually perpendicular axes of suspension, by finding the period of oscillation in the magnetic field and in zero field. The values obtained were $0{\cdot}012 \times 10^{-6}$, $0{\cdot}01 \times 10^{-6}$ and $0{\cdot}003 \times 10^{-6}$ per gm. These values are very small compared with the magnetic susceptibility and hence the specimen can be taken to be magnetically isotropic.

The magnetic susceptibility was measured by a Curie balance and was found to be $7{\cdot}78 \times 10^{-6}$ per gm. at 25° C. It was found to be independent of the field strength within the limits of experimental accuracy.

The specific gravity was found to be 2·448.

3. Discussion

The results indicate that the specimen is in the nature of a tektite which is known to be a glass-like material and except in one doubtful case mentioned in the literature shows no signs of crystallization. The magnetic isotropism of the specimen is in agreement with this fact which was further confirmed by Dr. R. S. Krishnan who studied it by the X-ray method and found it to have an amorphous structure. From the Brewsterian angle for the reflection at the polished surface, he had also estimated its refractive index as 1·535.

The tektites obtained from different localities are strikingly similar in their chemical composition, and the proportion of the different constituents especially the paramagnetic elements varies only within a fairly narrow range. The chemical analyses of a number of specimens are reported by Spencer (1939). Most of them contain from 68 to 80% of silica, about 10 to 15% of aluminium oxide and a small percentage of the oxides of the alkali-metals and the alkaline earths. Iron is the chief paramagnetic constituent being present in it both as ferrous and ferric oxides. The ferrous oxide content varies up to a maximum of about 7%, while the ferric oxide is comparatively small, less than one per cent. in most cases. Nickel and chromium are the other paramagnetic elements found in it and the analyses of Preuss (1934, 1935) show that they are present only in very small quantities. Since the proportion of iron varies only within a narrow range and it is present mostly as ferrous oxide, it is possible to make a rough estimate of the iron content from the magnetic susceptibility and compare it with the results of the chemical analyses reported. Spencer's report also shows that as the percentage of silica increases from 68 to 80%, the specific gravity progressively decreases from about 2·50 to about 2·34. The observed specific gravity of 2·448 corresponds roughly to 70% of silica. Assuming that all the iron is in the ferrous state and that 70% of the specimen is silica, the observed susceptibility is calculated to be due to 4·6% of ferrous iron which corresponds to 5·8% of ferrous oxide. In the calculation the spin-only value of 4·9 Bohr magnetons is used for the magnetic moment of the ferrous ion: correction for the diamagnetism of only 70% of silica is made assuming the value $-0{\cdot}493 \times 10^{-6}$ per gm. for its susceptibility.

The tektites occurring in the East Indies are known as billitonites. Their shape and surface corrugations suggest that they are presumably of

meteoric origin. The analysis of a typical billitonite is that it contains 70·92% silica, 1·04% ferric and 5·42% ferrous oxides. The observations of density and magnetic susceptibility thus give for the silica and the iron contents values of the same order as those quoted above for a billitonite.

In conclusion, the author wishes to record his deep sense of gratitude to Prof. Sir C. V. Raman for his keen interest and encouragement in this work.

4. *Summary*

The magnetic susceptibility and anisotropy and the specific gravity of a sample of tektite obtained from the island of Billiton, were determined. The magnetic susceptibility was $7{\cdot}78 \times 10^{-6}$ per gm. at 25° C. and it was magnetically isotropic. The specific gravity was 2·448. By a rough calculation from its magnetic susceptibility the amount of ferrous oxide present in it is estimated to be 5·8%. These observations are in agreement with the known structure and composition of the tektites.

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INTERFEROMETRIC STUDIES OF LIGHT SCATTERING IN BINARY LIQUID MIXTURES—PART II

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Received June 9, 1944

(Communicated by Sir C. V. Raman, Kt., F.R.S., N.L.)

1. *Introduction*

In a previous communication to these *Proceedings*, the author (1943) has reported the results of a spectro-interferometric investigation of the light scattered by binary liquid mixtures of both miscible and immiscible types. It emerged from these studies that the size of the ultimate particles of these mixtures plays a fundamental role in the appearance or otherwise of the Brillouin components, as well as their intensity relative to the central component. The absence of the shifted components in the interferometric patterns of the light scattered by critical mixtures both at and above their critical temperatures was interpreted as indicating the existence of molecular aggregates in them of size comparable to the wave-length of sound waves not only at their critical solution temperatures, but also at temperatures considerably removed from them, thus preventing the free propagation of sound waves.

An interferometric study of the light scattered by these mixtures thus affords a new method for the detection of molecular aggregates in them. Such a study has been undertaken in the present communication for a series of phenol-water mixtures having different compositions at different temperatures with a view to ascertain the influence of composition and of temperature on the formation of these molecular aggregates.

2. *Experimental Details*

The high scattering power of phenol-water mixtures, the wide range of temperatures afforded by them for investigation as well as the large displacements of the Brillouin components shown by their individual component liquids make them highly suitable for the study of the effect of composition on the formation of clusters. Pure freshly distilled phenol was mixed in the requisite proportion with double distilled water and the mixture directly transferred into a flask of capacity 400 c.c. The flask was connected to a Wood's tube of nearly 250 c.c. capacity having a length of 20 cm. and

diameter 3 cm. The flask was immersed in ice and the system sealed off in vacuum. The mixture was then obtained dust free in the Wood's tube by repeated slow distillation and the latter sealed off. Seven different mixtures of phenol-water containing respectively (*a*) 10%, (*b*) 15%, (*c*) 28%, (*d*) 34%, (*e*) 60%, (*f*) 70% and (*g*) 80% by weight of phenol were prepared in the manner indicated above, the capacity of the experimental tubes being approximately the same in all cases. The rest of the procedure was similar to that given in a previous paper.

The exposure employed to register the interferometric patterns for all the mixtures at a given temperature was identical.

3. *General Statement of Results*

The interference patterns of a series of seven phenol-water mixtures for the 4810 A.U. line of the zinc-mercury amalgam arc obtained with a 5 mm. separation for the etalon are reproduced in Fig. 1 (*d*) to (*s*) while Fig. 1 (*a*), (*b*), (*c*) gives the patterns obtained for the component liquids by Venkateswaran (1942). As can be seen from these photographs, water clearly shows all the three components, the central component being slightly weak in comparison to the outer ones. The Brillouin shift for water is $0{\cdot}28\ \text{cm.}^{-1}$, the velocity of sound propagation being 1509 m/sec. Phenol, on the other hand, at 42° C. gives two sharp shifted components of very low intensity. As the temperature is raised to 162° C. these components gain in intensity, the sharpness, however, remaining unaffected. The central component exhibits a marked decrease in intensity and a continuum appears connecting the central and the Brillouin components. The critical mixture, (temperature of miscibility 69° C.) [see Fig. 1 (*g*)] however, shows no trace of the Brillouin components in spite of the fact that the pattern is heavily exposed. This result fully confirms similar behaviour reported by the author (1943) for the two critical mixtures considered in a previous communication.

The main features of the patterns obtained for the seven mixtures are the following:—

(1) The central component, for the mixtures containing 34%, 28%, 15% and 60% by weight of phenol appears with enormous intensity and breadth at 80° C.; these two factors showing a direct dependence on the composition of the mixture. The intensity as well as the width of the line is a maximum for the mixture having the exact critical composition while both these factors show a marked fall when the composition differs even by a small amount from the latter, the decrease being in the order stated above.

On the other hand, the unmodified line for the other three mixtures (*viz.*, mixture containing 10%, 70% and 80% of phenol) appears relatively weaker and sharper than in the former four mixtures.

(2) The effect of rise of temperature on the central component, in general, is to diminish its intensity and breadth, the decrease being less pronounced in the case of the critical composition mixture and more marked in others.

(3) The Brillouin components are absent in two mixtures (*viz.*, 34% and 28%) even when their temperatures were raised by about 80° C. above their critical temperatures; whereas for mixtures containing 15% and 60% phenol they are clearly though weakly seen at 150° C. [(See Fig. 1 (*f*) and (*o*)]

(4) In the case of the three mixtures, having 80%, 70% and 10% phenol by weight, the Brillouin components are present even at 80° C. The ratio of the intensity of the Brillouin components to the central component shows a marked increase with a rise in the percentage of phenol in the mixture.

(5) The shifted components gain considerably in intensity as the temperature of these mixtures is raised, this effect being very pronounced in the case of the mixture having the largest percentage of phenol.

4. Discussion of the Results

One of the striking results noticed in the present investigation is the appearance of the central component with enormous intensity and breadth in some of the mixtures. These two factors, however, appear to be closely related to the composition of the mixture and also its temperature of complete miscibility. Thus the intensity as well as the breadth of the central component is a maximum for the mixture having the exact critical composition, which as is well known has also a maximum temperature of complete miscibility (69° C.). They however diminish rapidly as we go away from the critical composition mixture in either direction in the order of composition given by 28%, 15%, 60%, 10%, 70% and 80% by weight of phenol which is also the order of their temperatures of miscibility.

Another observation which appears to be closely related to the one mentioned above is the non-appearance of the Brillouin components in the interference patterns of the mixtures having the following compositions, *viz.*, 34%, 28%, 15% and 60% at 80° C. and the appearance of the same though with feeble intensity in the other three mixtures, *viz.*, 80%, 70% and 10% at the same temperature.

These two results taken together clearly demonstrate the presence of large molecular clusters of size comparable to the wave-length of light in

the mixtures having 34%, 28%, 15% and 60% by weight of phenol. The enormous intensity and breadth of the central component stands easily explained on this basis as due to the whole intensity of the scattered light falling on the central component.

The presence of the shifted components on the other hand in the other three mixtures (*viz.*, 80%, 70%, 10%) taken together with the diminution in intensity and breadth of the central component in these mixtures indicate that there is a detectable proportion of molecular aggregates whose size is small compared to the wave-length of light.

Further, the marked increase in the intensity of the Brillouin components accompanied by a diminution in the intensity of the central component at higher temperatures suggests the breaking up of the molecular aggregates into smaller groups, a part of the intensity of the central component getting released during this process and being divided between the two Brillouin components.

An investigation of the effect of temperature on these mixtures indicated the presence of large molecular clusters for a range of 80° C. above their critical solution temperature for the mixtures containing 34% and 28% by weight of phenol and a range of 60° C. for mixtures having 15% and 60% by weight of phenol. The tendency for the formation of molecular clusters as well as the size of the clusters was found to be a maximum for the mixture having the exact critical composition.

5. *Relation to X-Ray and Other Optical Evidences*

Krishnamurthi (1929) has carried out X-ray diffraction studies for four phenol-water mixtures having the following compositions, *viz.*, 1 : 1, 1 : 2, 1 : 3 and 1 : 5. For pure phenol he reports two diffraction rings, the inner one being very faint. In 1 : 1 solution the phenol ring was observed in the same place as that for the pure liquid and a very weak and diffuse water ring at the same angle as that for water. In 1 : 2 solution the water ring was observed to gather in intensity while the phenol ring remained in the same place. For 1 : 3 solution the phenol ring appeared to be very weak and diffuse, while it could not be detected in 1 : 5 solution.

The tendency for the formation of two distinct rings at approximately the same angles as that for the component liquids was explained by him by postulating the formation of large molecular clusters of the individual components in the mixture. The present interferometric evidence fully supports this point of view.

Recently R. S. Krishnan (1935) undertook a systematic study of the intensity as well as the state of polarisation of the light scattered by a series of six phenol-water mixtures containing the following percentage weight of phenol 15%, 28%, 34%, 50%, 60%, 70%. The following important results emerged from his studies:

(1) For a mixture having any composition the depolarisation ratio is a minimum at the critical solution point, the intensity of transversely scattered light being a maximum.

(2) The depolarisation ratio attains the minimum value for the series for the mixture having the exact critical composition, the intensity also attaining the maximum value in this case.

(3) ρ_h (the depolarisation ratio with the incident light polarised with its electric vector horizontal) has a limiting value of 100% for mixtures containing 60% and 70% by weight of phenol thereby indicating that detectable clusters are not present in these mixtures while the fall in the value of ρ_h from 100% in the other three mixtures (*viz.*, 28% phenol, 34% phenol and 50% phenol) show the presence of detectable clusters in these.

(4) For 34% phenol mixture the range over which the clusters are observable is 30° C. while that for 28% phenol and 50% phenol it is less than 20° C.

(5) The tendency for the formation of molecular clusters as well as the size of the molecular clusters is found to be a maximum for the critical composition mixture. The present interferometric investigation has completely confirmed all the foregoing points excepting the fact that the range over which the clusters could be detected by the present technique was found to be much larger in all the mixtures than that reported by Krishnan. This may partly be explained on the basis that the present method is able to detect the heterogeneity of the mixture much earlier than that is possible by Krishnan's technique.

In conclusion, the author wishes to record her grateful thanks to Prof. Sir C. V. Raman for his kind interest and inspiring guidance.

6. *Summary*

A comparative spectro-interferometric study has been made of the intensity of light scattered by a series of seven phenol-water mixtures. The Brillouin components are absent in the case of four mixtures having 34%, 28%, 15% and 60% by weight of phenol thereby indicating the presence of large molecular clusters of size comparable to the wave-length of sound

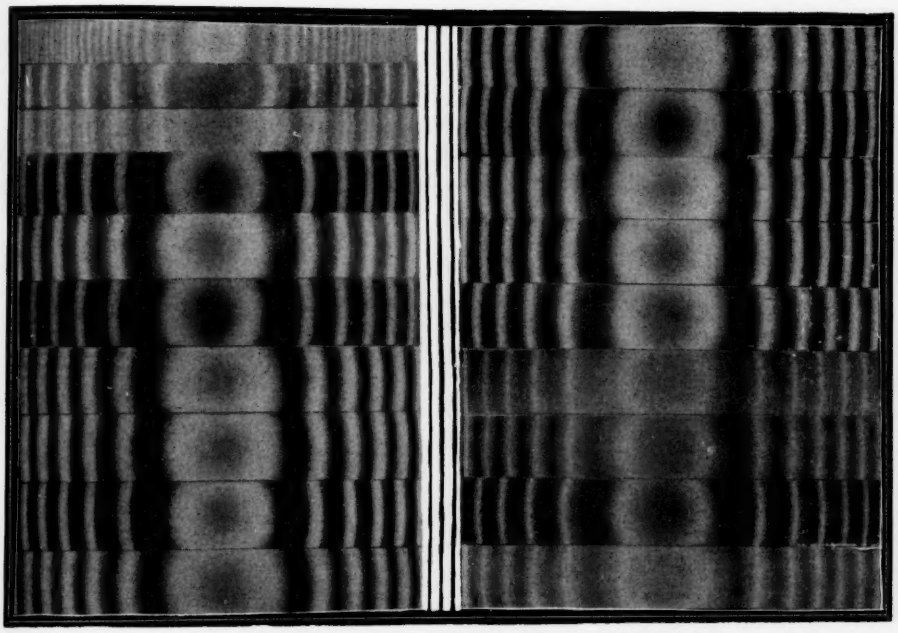

FIG. 1. Interferometric Patterns of Light Scattering in Mixtures

(*a*) Water (30° C.)
(*b*) Phenol (42° C.)
(*c*) ,, (162° C.)
(*d*) Phenol-Water Mixture 10% (80° C.)
(*e*) ,, ,, 15% (80° C.)
(*f*) ,, ,, ,, (150° C.)
(*g*) ,, ,, 34% (80° C.)
(*h*) ,, ,, ,, (120° C.)
(*i*) ,, ,, ,, (150° C.)
(*j*) ,, ,, 28% (80° C.)
(*k*) Phenol-Water Mixture 28% (120° C.)
(*l*) ,, ,, ,, (150° C.)
(*m*) ,, ,, 50% (80° C.)
(*n*) ,, ,, (120° C.)
(*o*) ,, ,, ,, (150° C.)
(*p*) ,, ,, 70% (120° C.)
(*q*) ,, ,, ,, (150° C.)
(*r*) ,, ,, 80% (120° C.)
(*s*) ,, ,, ,, (150° C.)

waves in them. In mixtures containing 80%, 70% and 10% by weight of phenol the shifted components are weakly present at 80° C. which shows that a detectable proportion of smaller sized clusters are present in them. On raising the temperature of these mixtures the Brillouin components increased in intensity indicating the breaking up of the large molecular clusters into smaller groups. The range over which the molecular clusters were detectable was 80° C. for the critical composition mixture while it was 60° C. for some others. The tendency for the formation of the molecular aggregates as well as the size of the aggregate was found to be a maximum for the critical composition mixtures. These results are found to be in agreement with X-ray and other optical evidences obtained for the same mixtures.

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THE SPECIFIC HEAT OF METALS CRYSTALLISING IN THE CUBIC SYTEM

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1. Introduction

It is now generally recognized that the Debye theory of specific heat is less successful in describing the thermal behaviour of metals than was formerly supposed. The failure of the theory is most obvious in particular cases, *viz.*, tungsten, lithium and gold. But even for those metals where it had been previously thought to be adequate, systematic deviations from the Debye formula have been brought to light by new and more accurate measurements over a wide range of temperatures (Ruhemann, 1937; Giaque and others, 1941). These facts can scarcely be regarded as surprising when we consider the nature of the assumptions on which the theory is based and especially the fact that it does not take into account the details of the crystal structure of the solid. The alternative theory of Born and Karman (1912) does consider the lattice structure of the crystal, but its physical background is closely analogous to that of the Debye theory and is open to objections of a similar character. It is a fact of observation that while elastic waves travel with high velocities through a solid, thermal energy does not, and indeed only diffuses with extreme slowness. Hence, the assumption made in both theories, that the modes of atomic vibration are determined by the external dimensions of the solid in the same way as in the familiar theory of elastic vibrations, is clearly not justified. It should also be pointed out that the nature of the atomic vibration spectrum deduced from these theories is irreconcilable with the observed spectroscopic facts. It is sufficient in this connection to refer to the cases of rock-salt and diamond in which the nature of the vibration spectrum has been very fully investigated (R. S. Krishnan, 1943, 1944).

A new theory of the specific heat of crystalline solids has been recently put forward by Sir C. V. Raman (1941, 1943). The present author has

already shown that the specific heat data of rock-salt and of diamond are in excellent accord with the results deduced on the basis of this theory. In the present paper, the investigation is extended to the case of nine metals crystallising in the cubic system. Of these five, namely, aluminium, silver, gold, copper and lead, crystallise as face-centred cubic lattices, while the remaining four, *viz.*, lithium, sodium, potassium and tungsten, form body-centred structures. The basis of the choice of these metals is the availability of exact specific heat data as also the knowledge of the three elastic constants of the cubic crystals. These constants form the basis for the evaluation of the discrete frequencies appearing in the theory.

2. *Description of the Normal Modes*

(*a*) *Face-centred lattice.*—The structure consists of four interpenetrating simple cubic lattices. The unit cube has four atoms, three of which excluding the atom at the origin occupy the centre of its three faces. The smallest cell, however, is a rhombohedron (AB. . . . GH, Fig. 1) with one atom per cell. In any normal mode, the phases of vibration of the successive atoms along the three rhombohedral edges AB, AC and AE are either the same or opposite to each other. All the normal modes can therefore be described by writing down the different cases in which this condition is satisfied. If we use the notation of the earliest papers on the subject, $(- + +)$ implies that the phases of atoms along the first axis are alternately opposite to each other, and are the same for all the atoms along the other two axes; in other words the atoms in the plane ACEG formed by the second and third axes are all in phase, while those of the next parallel plane BFHD are in exactly opposite phases to those of the first plane. The same sign denotes three modes, in two of which the motion is transverse and in the third longitudinal to the planes. The first two are identical from symmetry conditions. The plane ACEG of the rhombohedron is an octahedral plane of the large cubic cell as are the other rhombohedral faces ABEF and ABCD. The plane EBC involved in the mode $(- - -)$ is also octahedral so that each of the four classes of vibrations $(+ + -)$, $(+ - +)$, $(- + +)$, $(- - -)$ gives rise to the same two frequencies one longitudinal and the other doubly degenerate transverse. The mode $(- - +)$ is a vibration of the plane BCFG (which is parallel to a cube face) against its neighbouring parallel planes on either side. The other two $(- + -)$, and $(+ - -)$ are also vibrations of the cube planes, while $(+ + +)$ represents the translation of the whole cell. All these results are collected below and were first obtained by Chelam (1943) and by Ramachandran (1943).

No.	Phase sign	Description of Mode	Degeneracy
ν_1	$(-++), (++-), (+-+)$ & $(---)$	Longitudinal vibration of the octahedral planes against the neighbouring parallel planes on either side	4
ν_2	,,	Same as above but direction of motion transverse to the plane	8
ν_3	$(--+), (+--)$ & $(-+-)$	Longitudinal vibrations of the cubic planes against the neighbouring parallel planes on either side	3
ν_4	,,	The same as above but transverse	6
	$+++$	Translations	3
		TOTAL ..	24

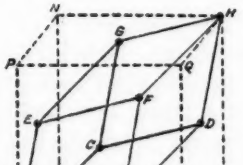

FIG. 1. Unit cell of a face-centred cubic lattice

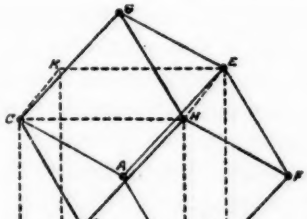

FIG. 2. Unit cell of a body-centred cubic lattice

(*b*) *Body-centred lattice.*—It consists of two interpenetrating simple cubic lattices, the atoms of one occupying the centre of the cubes of the other. The unit cell (AB....GH, Fig. 2) is again a rhombohedron, the three faces ABCD, ABEF and ACGE of which are all dodecahedral planes of the cube. The planes BCFG, CEFD and EBGD which pass through one axis of the rhombohedron and externally bisect the angle between the other two are also dodecahedral planes. All the six classes of vibrations excluding $(---)$ and $(+++)$, therefore involve the vibrations of the dodecahedral planes. Chelam (*l.c.*) and Ramachandran (*l.c.*) have shown from symmetry considerations that the two transverse vibrations of the dodecahedral planes are distinct from each other so that there are three frequencies corresponding to each of the above six types. $(---)$ is obviously a triply degenerate oscillation of the two interpenetrating cubic lattices against each other. The full results are collected below:

No.	Phase sign	Description of Mode	Degeneracy
ν_1	$(-++), (+-+), (++-), (--+), (+--)$ & $(-+-)$	Longitudinal vibration of the dodecahedral planes against the neighbouring parallel planes on either side	6
ν_2	,,	The same with direction of motion parallel to the cube axis in the plane	6
ν_3	,,	The same with direction of motion parallel to a face diagonal in the plane	6
ν_4	$(---)$	Vibration of the centre atom against the cube corners	3
	$+++$	Translations	3
		TOTAL ..	24

(*c*) *Nature of the three translations.*—The three translations give rise to slower vibrations in a larger repetition pattern, and ultimately pass over into pure elastic vibrations involving the boundary of the crystal. An analysis of these lower frequencies has not yet been made but is unnecessary from the point of view of evaluation of the thermal energy. At moderate and high temperatures the contribution of the slower vibrations to the thermal energy reaches its limiting value, and it is solely determined by the higher frequencies and their degeneracies. In the papers on the specific heats of rock-salt (*l.c.*) and diamond (*l.c.*) it has been shown that this part of the spectrum can be approximately identified with the elastic spectrum and can be conveniently represented by a Debye function. We will use the same method here. To take account of the reduced number $\left(\frac{3N}{8}\right)$ of the degrees of freedom belonging to this part of the spectrum, the usual characteristic temperature of the Debye theory is to be divided by $\sqrt[3]{8}$. In most cases the Debye θ has been taken from our previous calculation (unpublished) by the well-known Hopf and Lechner's method (1914).

3. *Equations of Motion and Frequencies*

(*a*) *Face-centred lattice.*—Every atom of the lattice is surrounded by twelve equidistant neighbours, whose co-ordinates relative to the atom at the origin are of the form $\pm\left(\frac{a}{2}\frac{a}{2}0\right)$ where a is the length of the cube edge. The next nearest neighbours are six in number and are found at a distance of $\pm a$ along each of the three cube axes. If we make use of the approximation that only neighbours and next nearest neighbours of an atom produce

effective forces on it, the most general equation of motion of the atom (0 0 0) can be written as follows. The forces are not necessarily central. The notation and symbols used here are similar to those adopted by Born and Karman (*l.c.*). These authors had considered a simple cubic lattice in which the neighbours are found along the cube edges and the next neighbours along the face diagonals. In our case the situation as regards the neighbours and the next neighbours is just the reverse but the form of the equation is unaltered. $u_{\frac{1}{2}\frac{1}{2}0}$, $v_{\frac{1}{2}\frac{1}{2}0}$, $w_{\frac{1}{2}\frac{1}{2}0}$ represent the displacements of the atom $\frac{1}{2}\frac{1}{2}0$ along the three co-ordinate axes respectively which have been taken parallel to the cube edges.

$$\begin{aligned} m\ddot{u}_{000} = \alpha\,[&u_{\frac{1}{2}\frac{1}{2}0} + u_{-\frac{1}{2}-\frac{1}{2}0} + u_{\frac{1}{2}-\frac{1}{2}0} + u_{-\frac{1}{2}\frac{1}{2}0} - 4u_{000} \\ &+ u_{\frac{1}{2}0\frac{1}{2}} + u_{-\frac{1}{2}0-\frac{1}{2}} + u_{\frac{1}{2}0-\frac{1}{2}} + u_{-\frac{1}{2}0\frac{1}{2}} - 4u_{000}] \\ + \delta\,[&u_{0\frac{1}{2}\frac{1}{2}} + u_{0-\frac{1}{2}-\frac{1}{2}} + u_{0\frac{1}{2}-\frac{1}{2}} + u_{0-\frac{1}{2}\frac{1}{2}} - 4u_{000}] \\ + \gamma\,[&v_{\frac{1}{2}\frac{1}{2}0} + v_{-\frac{1}{2}-\frac{1}{2}0} - v_{\frac{1}{2}-\frac{1}{2}0} - v_{-\frac{1}{2}\frac{1}{2}0} + w_{\frac{1}{2}0\frac{1}{2}} + w_{-\frac{1}{2}0-\frac{1}{2}} - w_{\frac{1}{2}0-\frac{1}{2}} - w_{-\frac{1}{2}0\frac{1}{2}}] \\ + \beta\,[&u_{100} + u_{-100} - 2u_{000}] + \chi\,[u_{010} + u_{0-10} + u_{001} + u_{00-1} - 4u_{000}] \quad (1) \end{aligned}$$

with the similar equations in v and w.

The formulæ for the frequencies can be obtained by substituting the displacements of the atoms in the equation (1). The designation of the frequencies given below is the same as given earlier and l denotes the displacement of the atom at the origin along the direction of motion

ν_1:—Let the direction cosines of motion be $\frac{1}{\sqrt{3}}, \frac{1}{\sqrt{3}}, \frac{1}{\sqrt{3}}$. Then

$$u_{-\frac{1}{2}\frac{1}{2}0} = u_{\frac{1}{2}-\frac{1}{2}0} = u_{-\frac{1}{2}0\frac{1}{2}} = u_{\frac{1}{2}0-\frac{1}{2}} = u_{0\frac{1}{2}-\frac{1}{2}} = u_{0-\frac{1}{2}\frac{1}{2}} = u_{000} = \frac{l}{\sqrt{3}}$$

All the other neighbours have $u = -u_{000} = -\frac{l}{\sqrt{3}}$

For the next nearest neighbours $u = -\frac{l}{\sqrt{3}}$ and $u = v = w$ for all the atoms. On substitution

$$m\ddot{l} = -[8\alpha + 4\delta + 4\beta + 8\chi + 8\gamma]\,l$$

$$\nu_1 = \frac{1}{2\pi}\sqrt{\frac{8\alpha + 4\delta + 4\beta + 8\chi + 8\gamma}{m}} \qquad (2)$$

ν_2:—Let the direction of motion be a face diagonal with cosines $\left(\frac{1}{\sqrt{2}} - \frac{1}{\sqrt{2}} 0\right)$. We have

$$u_{-\frac{1}{2}\frac{1}{2}0} = u_{\frac{1}{2}-\frac{1}{2}0} = u_{-\frac{1}{2}0\frac{1}{2}} = u_{\frac{1}{2}0-\frac{1}{2}} = u_{0\frac{1}{2}-\frac{1}{2}} = u_{0-\frac{1}{2}\frac{1}{2}} = u_{000} = \frac{l}{\sqrt{2}}.$$ For all of them $v = -\frac{l}{\sqrt{2}}$ and $w = 0$.

For all the other atoms $u = -\frac{l}{\sqrt{2}}$ $v = +\frac{l}{\sqrt{2}}$ $w = 0$

on substitution

$$m\ddot{l} = -(8\alpha + 4\delta - 4\gamma + 4\beta + 8\chi)\, l$$

$$\nu_2 = \frac{1}{2\pi}\sqrt{\frac{8\alpha + 4\delta - 4\gamma + 4\beta + 8\chi}{m}} \qquad (3)$$

ν_3:—Let the direction of motion be parallel to the X-axis.

Then

$u_{0\frac{1}{2}\frac{1}{2}} = u_{0-\frac{1}{2}-\frac{1}{2}} = u_{0\frac{1}{2}-\frac{1}{2}} = u_{0-\frac{1}{2}\frac{1}{2}} = u_{000} = l.$

All the other neighbours have $u = -l$. Next neighbours have $u = l$. $v = w = 0$ for all the atoms.

On substitution

$$m\ddot{l} = -16\alpha l \quad \nu_3 = \frac{1}{2\pi}\sqrt{\frac{16\alpha}{m}}. \qquad (4)$$

ν_4:—Let the direction of motion be the X direction and the plane of constant phase the XZ plane.

Then,

$$u_{\frac{1}{2}0\frac{1}{2}} = u_{\frac{1}{2}0-\frac{1}{2}} = u_{-\frac{1}{2}0\frac{1}{2}} = u_{-\frac{1}{2}0-\frac{1}{2}} = l.$$

All neighbours have $u = -l$ and the next neighbours $u = l$. $v = w = 0$ for all atoms.

$$m\ddot{l} = -8(\alpha + \delta)\, l \qquad \nu_4 = \frac{1}{2\pi}\sqrt{\frac{8(\alpha + \delta)}{m}} \qquad (5)$$

(*b*) *Body-centred lattice.*—There are eight equidistant neighbours of an atom whose co-ordinates relative to the origin atom are of the form $\pm\left(\frac{a}{2}, \frac{a}{2}, \frac{a}{2}\right)$. The next neighbours are the same as in the previous case. Proceeding as before the equation of motion can be written as below. $\Sigma u_{\frac{1}{2}\frac{1}{2}\frac{1}{2}}$ denotes the sum of u displacements of all the eight neighbours.

$$\begin{aligned} m\ddot{u}_{000} = {} & \alpha\,[\Sigma u_{\frac{1}{2}\frac{1}{2}\frac{1}{2}} - 8u_{000}] \\ & + \gamma\,[v_{\frac{1}{2}\frac{1}{2}\frac{1}{2}} + v_{-\frac{1}{2}-\frac{1}{2}-\frac{1}{2}} + v_{\frac{1}{2}\frac{1}{2}-\frac{1}{2}} + v_{-\frac{1}{2}-\frac{1}{2}\frac{1}{2}} - v_{\frac{1}{2}-\frac{1}{2}\frac{1}{2}} - v_{-\frac{1}{2}\frac{1}{2}-\frac{1}{2}} - v_{\frac{1}{2}-\frac{1}{2}-\frac{1}{2}} - v_{-\frac{1}{2}\frac{1}{2}\frac{1}{2}} \\ & + w_{\frac{1}{2}\frac{1}{2}\frac{1}{2}} + w_{-\frac{1}{2}-\frac{1}{2}-\frac{1}{2}} + w_{\frac{1}{2}-\frac{1}{2}\frac{1}{2}} + w_{-\frac{1}{2}\frac{1}{2}-\frac{1}{2}} - w_{\frac{1}{2}\frac{1}{2}-\frac{1}{2}} - w_{-\frac{1}{2}-\frac{1}{2}\frac{1}{2}} - w_{\frac{1}{2}-\frac{1}{2}-\frac{1}{2}} - w_{-\frac{1}{2}\frac{1}{2}\frac{1}{2}}] \\ & + \beta\,[u_{100} + u_{-100} - 2u_{000}] \\ & + \chi\,[u_{010} + u_{0-10} + u_{001} + u_{00-1} - 4u_{000}] \end{aligned} \qquad (6)$$

with the similar equations in v and w.

ν_1:—

Let the direction cosines of motion be $\frac{1}{\sqrt{2}}\ \frac{1}{\sqrt{2}}\ 0$. Then

$$u_{\frac{1}{2}\frac{1}{2}\frac{1}{2}} = u_{-\frac{1}{2}-\frac{1}{2}-\frac{1}{2}} = u_{\frac{1}{2}\frac{1}{2}-\frac{1}{2}} = u_{-\frac{1}{2}-\frac{1}{2}+\frac{1}{2}} = \frac{-l}{\sqrt{2}}$$

other nearest neighbours have $u = \frac{l}{\sqrt{2}}$. Amongst the next neighbours

$$u_{100} = u_{-100} = u_{010} = u_{0-10} = \frac{-l}{\sqrt{2}}$$

and $$u_{001} = u_{00-1} = \frac{l}{\sqrt{2}}$$

All the atoms have $u = v$ and $w = 0$.

On substitution,

$$m\ddot{l} = -(8\alpha + 4\beta + 4\gamma + 4\chi)\, l$$

$$\nu_1 = \frac{1}{2\pi}\sqrt{\frac{8\alpha + 4\beta + 4\gamma + 4\chi}{m}} \tag{7}$$

ν_2:—

Let the direction of motion be parallel to the X-axis, and the dodecahedral plane be the one containing this axis (plane LBKE, Fig. 2). The origin is at the atom A at the centre of the cube. Then,

$$v = w = 0 \text{ for all the atoms}$$

$$u_{\frac{1}{2}\frac{1}{2}\frac{1}{2}} = u_{-\frac{1}{2}-\frac{1}{2}-\frac{1}{2}} = u_{-\frac{1}{2}\frac{1}{2}\frac{1}{2}} = u_{\frac{1}{2}-\frac{1}{2}-\frac{1}{2}} = u_{100} = u_{-100} = u_{000} = l.$$

For the others $u = -l$.

On substitution

$$m\ddot{l} = -8l(\alpha + \psi) \quad \nu_2 = \frac{1}{2\pi}\sqrt{\frac{8(\alpha + \psi)}{m}} \tag{8}$$

ν_3:—

Let the direction of motion have cosines $-\frac{1}{\sqrt{2}}, \frac{1}{\sqrt{2}}$, 0 and the dodecahedral plane be the one passing through the Z-axis.

$$w = 0 \text{ and } v = -u \text{ for all the atoms}$$

$$u_{\frac{1}{2}\frac{1}{2}\frac{1}{2}} = u_{-\frac{1}{2}-\frac{1}{2}-\frac{1}{2}} = u_{\frac{1}{2}\frac{1}{2}-\frac{1}{2}} = u_{-\frac{1}{2}-\frac{1}{2}\frac{1}{2}} = u_{100} = u_{-100} = \frac{l}{\sqrt{2}}.$$

For the others $u = -\frac{l}{\sqrt{2}}$.

On substitution

$$m\ddot{l} = -(8\alpha + 4\beta - 8\gamma + 4\psi)$$

$$\nu_3 = \frac{1}{2\pi}\sqrt{\frac{8\alpha + 4\beta + 4\psi - 8\gamma}{m}} \tag{9}$$

ν_4:—

Let the direction of motion be parallel to X-axis; then $u = -l$ for all the neighbours and $+l$ for the next neighbours.

$$m\ddot{l} = -16(\alpha l) \quad \nu_4 = \frac{1}{2\pi}\sqrt{\frac{16\alpha}{m}}. \tag{10}$$

4. Correlation between the Force and the Elastic Constants

At present we have no experimental means of obtaining the vibration frequencies of metals, so that only indirect methods of correlating them to certain observed properties can be adopted. It has long been known that the forces produced in the elastic deformations of a solid are of the same nature as are involved in its internal vibrations. The well-known methods of Madelung (1910), Sutherland (1911), Einstein (1911), Born and Karman (1912) and Debye (1912) sought a correlation between the elastic properties and the frequency spectrum of a solid. The elastic constants of metallic crystals, however, depend to a certain extent also on factors other than the interatomic forces such as impurities, conditions of growth, mosaicity, and the elastic history of the specimen. Unfortunately the elastic data of the metallic crystals are very meagre and no attempts seem to have been made to eliminate the effects of the external conditions of the material. While the individual experimenters have claimed a high degree of accuracy for their measurements, the differences between the observed values of different workers, wherever available, are quite large (10–20%). Zwicky (1924) who made a detailed review of the data then obtainable, came to the conclusion that this is due to the fact that the crystals used are not elastically identical. Hansom (1934) worked with the single crystals of zinc 99·99% pure but obtained from different sources and found that there was a difference of about 30% in the compressibilities of the two specimens. In a similar way the shear constant c_{44} of the single crystals of copper as measured by Goens and Weets (1932) differs from a similar measurement of Kimura (1933) by about 25%.

The thermal energy on the other hand is not so sensitive to the elastic history and other accidental conditions of growth, etc., and seems to depend entirely on the interatomic forces. A discussion as to whether the specific heats of metals are sensibly influenced by cold working, crystallisation, etc., has been given in many places, Eucken (1929), Eucken and Werth (1930), Maeir and Anderson (1934) and Giaque, etc. (1941). The difference, if any, between the specific heats of the samples differently treated is generally of the order of 1%. It follows, therefore, that only approximate values of the frequencies can be obtained from the elastic properties, though the correlation is close enough to show the general trend of the thermal energy curves of the two crystallographic systems under study.

In the following we will use the Born and Karman (*l.c.*) method for connecting the elastic and the force constants.

(*a*) *Face-centred lattice.*—On replacing the differences by the differential coefficients in the equation (1) by the use of Taylor's theorem, we pass to the limiting case of the continuum. Since the density ρ is $\frac{4m}{a^3}$, we have on multiplying both sides by $\frac{4m}{a^3}$ and replacing the differences by the differential coefficients

$$\frac{4m\ddot{x}}{a^3} = \rho X$$

$$= \frac{1}{a}\left\{4(\alpha+\beta)\frac{\partial^2 u}{\partial x^2} + 2(\alpha+\delta+2\psi)\right.$$

$$\left.\left(\frac{\partial^2 u}{\partial y^2}+\frac{\partial^2 u}{\partial z^2}\right) + 4\gamma\left(\frac{\partial^2 v}{\partial x\partial y}+\frac{\partial^2 w}{\partial x\partial z}\right)\right\} \tag{11}$$

The corresponding equation for a continuum in terms of the elastic constants is

$$\rho X = c_{11}\frac{\partial^2 u}{\partial x^2} + c_{44}\left(\frac{\partial^2 u}{\partial y^2}+\frac{\partial^2 u}{\partial z^2}\right)$$

$$+ (c_{12}+c_{44})\left(\frac{\partial^2 v}{\partial x\partial y}+\frac{\partial^2 w}{\partial x\partial z}\right). \tag{12}$$

On comparing the coefficients

$$\left.\begin{aligned} ac_{11} &= 4(\alpha+\beta) \\ ac_{44} &= 2(\alpha+\delta+2\psi) \\ a(c_{12}+c_{44}) &= 4\gamma \end{aligned}\right\} \tag{13}$$

The three elastic coefficients are not enough to determine the five force constants. If the central forces are operative $\delta = \psi = 0$ and $\alpha = \gamma$ so that we obtain the well-known Cauchy relation $c_{12} = c_{44}$. This relation is not even roughly obeyed by any metal, the value of c_{12} being very often more than double c_{44}. We have, therefore, to use the full relations given in (13), with reasonable approximations. Following Born and Karman, we assume that the force due to a displacement perpendicular to the line joining any two atoms varies much more rapidly with the distance than the one due to a displacement parallel to it. We can in such a case assume ψ to be small and neglect it. A displacement perpendicular to the line joining any two nearest atoms can take place either along a face diagonal or parallel to a cube edge. Both these directions are not symmetrically equivalent so that the displacements along them can give rise to different forces. The actual values of these forces obviously lie between those obtained from the limiting cases (i) when both are equal, (ii) when one of them is zero and the other finite. Our calculations show that three frequencies come out to be the same whichever is the alternative adopted. Only the frequency of the

smallest statistical weight depends on the choice of the assumptions made and the difference is not usually very important from the specific heat standpoint. We can therefore safely assume that the displacements along either of the above two directions give rise to the same force-constants. It can be easily seen that in this case $\alpha - \gamma = \delta$. The force constants are accordingly given by

$$\alpha = \frac{3ac_{44} + ac_{12}}{8} \quad \beta = \frac{2ac_{11} - 3ac_{44} - ac_{12}}{8}$$

$$\delta = \frac{a(c_{44} - c_{12})}{8} \quad \gamma = \frac{2ac_{44} - ac_{12}}{8} \quad \psi = 0. \tag{14}$$

The frequencies are given by

$$\begin{aligned} \nu_1 &= \frac{1}{2\pi}\sqrt{\frac{4ac_{44} + 2ac_{12} + ac_{11}}{m}} \\ \nu_2 &= \frac{1}{2\pi}\sqrt{\frac{ac_{11} + ac_{44} - ac_{12}}{m}} \\ \nu_3 &= \frac{1}{2\pi}\sqrt{\frac{6ac_{44} + 2ac_{12}}{m}} \\ \nu_4 &= \frac{1}{2\pi}\sqrt{\frac{4ac_{44}}{m}} \end{aligned} \tag{15}$$

(*b*) *Body-centred metals.*—Proceeding as before we get

$$\left.\begin{aligned} ac_{11} &= 2(\alpha + \beta) \\ ac_{44} &= 2\alpha + 2\psi \\ a(c_{12} + c_{44}) &= 4\gamma \end{aligned}\right\} \tag{16}$$

As before we put $\psi = 0$ and get the following expressions for the frequencies.

$$\begin{aligned} \nu_1 &= \frac{1}{2\pi}\sqrt{\frac{4ac_{44} + 2ac_{12} + 2ac_{11}}{m}} \\ \nu_2 &= \frac{1}{2\pi}\sqrt{\frac{4ac_{44}}{m}} \\ \nu_3 &= \frac{1}{2\pi}\sqrt{\frac{2a(c_{11} - c_{12})}{m}} \\ \nu_4 &= \frac{1}{2\pi}\sqrt{\frac{8ac_{44}}{m}} \end{aligned} \tag{17}$$

It will be seen that the three frequencies of each system comprising eighteen out of a total of twenty-one optical degrees of freedom are very closely related to the elastic wave velocities in the crystal along the direction of propagation of the corresponding vibrations. We can get the same

expression by dividing the wave velocity by the appropriate wave-length and multiplying the result by a dispersion factor $\frac{2}{\pi}$. This factor was first obtained theoretically by Born and Karman (*l.c.*) for a unidimensional lattice and also for the waves travelling along the axes in a simple cubic lattice. The occurrence of this factor arises, however, in their case as in ours from the approximations used in deriving the force field. In a general case the dispersion law is likely to be more complicated.

According to Fuchs (1936), the failure of the Cauchy relations is due to the fact that the compressibility involves the kinetic and a part of the potential energy of the electrons, which do not enter into the calculations of $c_{11}-c_{12}$ and c_{44}. Fine (1939) in his work on the specific heat of tungsten eliminated the contribution of electrons by reducing the observed c_{11} and c_{12} in such a way that the difference $c_{11}-c_{12}$ was not altered and the Cauchy relation was satisfied. Fuchs' calculations were, however, concerned with those metals where the departure from the Cauchy relations was not so large as for most of the metals which are the subject of discussion in this paper. He used the well-known Born and Mayer (1932) expression for the repulsive potential between the ions in order to calculate the elastic constants of the alkali metals. In the alkali halides this assumption again gives rise to the Cauchy relation which they do not obey at the low temperatures. Seitz (1940) has pointed out that this is due to the fact that the repulsive potential is not spherically symmetrical and is not given accurately by the Born and Mayer expression. Owing to the negligible contribution from this source to the elastic constants of alkali metals it does not very much matter there. The mutual interaction of the ions, however, plays the most predominant part in the compressibilities of the noble metals (Fuchs, 1935), so that the very large deviation from the Cauchy relation in their cases (probably in the case of aluminium and lead also) is more likely due to the lack of spherical symmetry in the mutual ionic potential. If this is so, a displacement normal to the line joining the atoms will give rise to sensible forces. We believe, therefore, that the force model adopted here is a closer approximation to the actual forces than the one adopted by Fine.

5. *Evaluation of the Atomic Heats*

Both the Einstein and Debye functions reach their limiting values at the high temperatures where a small change in the frequency does not cause any sensible change in the values of the functions. As we go lower in the temperature scale the sensitiveness of the functions to the changes of frequency increases gradually and becomes very large at the low temperatures.

It is well known that the elastic constants of solids show a large increase at low temperatures so that the frequencies calculated from the room temperature data would give quite erroneous values of the specific heats at low temperatures. If, on the other hand, the low temperature elastic data are employed for this purpose, the high temperature specific heats will not show large errors because of the relative insensitiveness of the functions in that region. In the following calculations we will use the low temperature elastic data wherever it is possible to do so. The expression for c_v according to the present theory is

$$c_v = \frac{3R}{24}\left[\sum_1^4 n_s \, E\left(\frac{h\nu_s}{kT}\right) + 3\,D\left(\frac{\theta}{T}\right)\right], \qquad (18)$$

where n_s is the number of degrees of freedom corresponding to the frequency ν_s and E and D stand for the Einstein and Debye functions, respectively. θ_D is the Debye characteristic temperature reduced for smaller degrees of freedom as described earlier. In view of the approximations of the force model adopted here we have also given the calculations from an empirical set of frequencies in which the lowest frequency has been changed empirically whilst the others retain their theoretical values. In the case of sodium where the uncertainty in measured elastic constants is very large, one of the highest frequencies has also been empirically altered. The calculations so made have been entered as II set in the following tables.

(*a*) *Face-centred lattice*: (i) **Aluminium.**—The elastic constants of aluminium at the room temperature are (Goens, 1933) in units of 10^{11} dynes/cm^2.

$$c_{11} = 10{\cdot}82 \qquad c_{12} = 6{\cdot}22 \qquad c_{44} = 2{\cdot}84$$

Goens had earlier (1929) given the temperature coefficients of the Torsion and elasticity modulii relative to a few planes in the crystal. An approximate calculation with the above constants yields the following data for 20°K.

$$c_{11} = 12{\cdot}2 \qquad c_{12} = 6{\cdot}9 \qquad c_{44} = 3{\cdot}22$$

The Debye characteristic temperature as calculated by us from the room temperature data by Hopf and Lechner's method is 410. If we use Blackman's approximate formula (1935) $\theta_D^3 \propto \sqrt{c_{11}c_{44}^2}$ to find out the order of change at the low temperature, θ_D is 437 at the liquid hydrogen temperatures. In order to take the reduced degrees of freedom into account the elastic spectrum in the present work has to be represented by $\frac{437}{\sqrt[3]{8}} = 219°$ K. The calculated values of frequencies and the atomic heats are given in the tables I(*a*) and I (*b*). In view of the fact that the Debye formula is generally used

with an empirical constant we have shown the specific heats calculated from the theoretical θ (437) also in the last column of Table I (*b*).

TABLE I (*a*)

Vibration frequencies of aluminium

	ν_1	ν_2	ν_3	ν_4	Reduced θ_D
Calculated from elastic data cm.$^{-1}$	313	147	290	180	..
.. .. .. $\frac{h\nu}{k}$	449	210	416	258	219
II set (ν_2 empirical) $\frac{h\nu}{k}$	,,	245	,,	,,	,,

TABLE I (*b*)

Specific heats of aluminium, cals./deg. gm. atom

Experimental data of Giaque, etc. (1941 *a*)

Temperature ° K.	Calculated c_v I set: Optical frequencies	Elastic spectrum	Total c_v	Calculated c_v II set	Experimental c_v	c_v (Debye) $\theta = 437$
15	..	·019	·019	·019	·022	·0187
20	·006	·043	·049	·045	·054	·044
30	·109	·129	·238	·187	·203	·180
40	·391	·235	·626	·499	·500	·351
50	·793	·333	1·126	·946	·912	·654
80	2·035	·526	2·561	2·371	2·298	1·894
100	2·676	·593	3·269	3·109	3·094	2·677
120	3·218	·633	3·851	3·733	3·704	3·306
160	3·890	·679	4·569	4·487	4·536	4·18
200	4·300	·701	5·001	4·937	5·039	4·749
300	4·761	·725	5·486	5·466*	5·59	5·368

(ii) **Silver.**—The elastic data at low temperatures are unknown. The room temperature values according to Röhl's measurements (1933) are in 10^{11} dyne/cm.^{2}

$$c_{11} = 12{\cdot}0 \qquad c_{12} = 9{\cdot}0 \qquad c_{44} = 4{\cdot}36$$

Grüneisen (*cf. Handbuch der Physik*, Vol. X) has given a relation connecting the changes in frequencies (and therefore indirectly the changes in elastic constants) with the thermal expansion and Grüneisen's constant γ. The values of γ for aluminium and silver as given by him are 2·17 and 2·4 respectively. The thermal coefficients of expansion are also approximately the same being ·000018 for aluminium from (− 196 to 0° C.) and (·0000176) for silver from (− 102 to 0° C.). We are therefore justified in making the

assumption that the percentage change of elastic constants for a given change of temperature is the same in both cases. Under these conditions the elastic data become

$$c_{11} = 13{\cdot}6 \qquad c_{12} = 9{\cdot}9 \qquad c_{44} = 4{\cdot}94$$

The Debye θ calculated by Hopf and Lechner's method is 227 and becomes 240 after allowing for change of temperature. The reduced θ_D is accordingly 120. The frequencies and the atomic heats are given in Tables II (*a*) and II (*b*) respectively.

TABLE II (*a*)

Vibration frequencies of silver

	ν_1	ν_2	ν_3	ν_4	Reduced θ_D
Calculated from elastic constants cm.$^{-1}$	185	74	178	113	..
.. .. .. $\frac{h\nu}{k}$	265	108	258	162	120
II set (ν_2 empirical) $\frac{h\nu}{k}$	,,	120	,,	,,	,,

TABLE II (*b*)

Specific heats of silver, cals/deg. gm. atom

Experimental data of Giaque, etc. (1941 *b*)

Temperature °K.	Calculated c_v I set			Calculated c_v II set	Experimental c_v
	Optical frequencies	Elastic spectrum	Total c_v		
15	·081	·102	·183	·149	·160
20	·294	·198	·492	·406	·410
30	·962	·375	1·337	1·197	1·140
40	1·664	·493	2·157	2·058	2·001
50	2·289	·568	2·857	2·748	2·776
60	2·799	·615	3·414	3·325	3·405
100	4·017	·694	4·711	4·665	4·769
150	4·631	·721	5·352	5·325	5·391
200	4·859	·731	5·590	5·576	5·653
300	5·050	·740	5·79	5·80	5·83

(iii) **Gold.**—Amongst the metals of this structure the specific heats of gold form the most conspicuous example of the failure of the Debye theory in the sense that no empirical Debye constant can predict any part of the specific heat curve successfully. The elastic constants as measured by Röhl (*l.c.*) at room temperature are (in 10^{11} dyne/cm.^{2}).

$$c_{11} = 18{\cdot}7 \qquad c_{12} = 15{\cdot}7 \qquad c_{44} = 4{\cdot}36$$

From the data given by Grüneisen (*l.c.*) it appears that the product of γ and the coefficient of expansion is almost the same as in the case of aluminium. We, therefore, assume that the percentage change in the elastic constants will be almost the same for both metals for the same fall of temperature. Allowing for the same we get at 20° K (in units of 10^{11} dyne/cm.^{2}).

$$c_{11} = 21{\cdot}13 \qquad c_{12} = 17{\cdot}27 \qquad c_{44} = 4{\cdot}93.$$

The Debye characteristic temperature as calculated from Hopf and Lechner's method is 171 and becomes 182 after allowing for the change due to fall of temperature. The reduced value is accordingly 91. The frequencies and the specific heats are given in Tables III (*a*) and (*b*) respectively.

TABLE III (*a*)

Vibration frequencies of gold

	ν_1	ν_2	ν_3	ν_4	Reduced θ_D
Calculated from elastic data cm.$^{-1}$	162	56	150	83	..
.. .. .. $\frac{kv}{k}$	233	80	215	119	91
II set (ν_3 empirical) $\frac{hv}{k}$ ..	,,	105	,,	,,	,,

TABLE III (*b*)

Specific heats of gold in cals./deg. gm. atom

Experimental data of Clusius and Harteck (1928)

Temperature ° K.	Calculated c_v I set			Calculated c_v II set	Experimental c_v
	Optical frequencies	Elastic spectrum	Total c_v		
14·96	·304	·193	·497	·315	·357
15·73	·365	·212	·577	·368	·431
20·33	·773	·323	1·096	·746	·782
24·9	1·201	·414	1·615	1·257	1·252
32·5	1·851	·519	2·370	2·031	1·998
44·0	2·632	·607	3·239	3·021	3·034
63·6	3·499	·674	4·173	4·056	4·143
82·5	4·058	·701	4·759	4·661	4·706
105·0	4·432	·717	5·149	5·085	5·124
147·5	4·780	·731	5·511	5·478	5·578
176·5	4·879	·735	5·614	5·589	5·706
212·5	4·999	·738	5·737	5·719	5·762

(iv) **Copper.**—The elastic constants as measured by Goens and Weets (*l.c.*) at the room temperature are in (10^{11} dynes/cm.^{2})

$$c_{11} = 17{\cdot}0 \qquad c_{12} = 12{\cdot}3 \qquad c_{44} = 7{\cdot}52$$

Measurements made by Kimura (*l.c.*) differ considerably from these and are

$$c_{11} = 17{\cdot}28 \qquad c_{12} = 11{\cdot}77 \qquad c_{44} = 6{\cdot}11$$

Fuchs (1936 (*a*) *l.c.*) has extrapolated Goens data to absolute zero by using the measurements of Grüneisen on the compressibility at different temperatures. His extrapolated values are

$$c_{11} = 18{\cdot}6 \qquad c_{12} = 13{\cdot}5 \qquad c_{44} = 8{\cdot}2$$

We have used the last data for the calculation of the frequencies. θ has also been calculated from the same data and comes to 377, the reduced θ being 189. The frequencies and atomic heats are given in Tables IV (*a*) and (*b*) respectively. In view of the fact that a major part of the difference between observed and calculated values at high temperatures is due to the use of low temperature elastic data we have not given the calculations from the empirical frequencies.

TABLE IV (*a*)

Vibration frequencies of copper

	ν_1	ν_2	ν_3	ν_4	Reduced θ_D
Calculated from elastic constants cm.$^{-1}$	275	113	271	178	..
$\frac{h\nu}{k}$	394	162	389	255	189

TABLE IV (*b*)

Specific heats of copper, cals./deg. gm. atom

Experimental data of Giaque, etc. (1941 *a*)

Temperature °K.	Calculated c_v			Experimental c_v
	Optical frequencies	Elastic spectrum	Total c_v	
15	·005	·029	·034	·041
20	·040	·066	·106	·114
30	·286	·179	·465	·412
50	1·166	·400	1·566	1·491
80	2·422	·573	2·995	3·077
100	3·043	·628	3·671	3·821
120	3·511	·660	4·171	4·339
160	4·125	·695	4·820	4·970
200	4·463	·712	5·175	5·323
300	4·853	·730	5·583	5·667

(v) **Lead.**—The elastic constants of single crystals of lead have been measured by Goens and Weets (1936) whose data as corrected for an arithmetical error by Lonsdale and Smith (1942) are (in 10^{11} dyne/cm.^{2})

$$c_{11} = 4{\cdot}77 \qquad c_{12} = 4{\cdot}03 \qquad c_{44} = 1{\cdot}44$$

No temperature coefficients of the elastic constants are known but our calculations show that the frequencies calculated from the room temperature data predict the course of the specific heat curve fairly well. It must be presumed that the combined effect of the approximations used and the uncertainty in the elastic constants partly balances the effect of temperature on the elastic constants. The Debye characteristic temperature calculated from the above constants is 103 from which the reduced value is 51. The frequencies and atomic heats are given in Table V (*a*) and (*b*) respectively.

TABLE V (*a*)

Vibration frequencies of lead

	ν_1	ν_2	ν_3	ν_4	Reduced θ_D
Calculated from elastic constants cm.$^{-1}$	87	30	82	48	..
$\frac{h\nu}{k}$	125	43	118	69	51

TABLE V (*b*)

Specific heats of lead, cals./deg. gm. atom

Experimental data of Giaque, etc. (1941 *b*)

Temperature °K.	Calculated c_v			Experimental c_v
	Optical frequencies	Elastic spectrum	Total c_v	
15	1·400	·445	1·845	1·727
20	2·116	·550	2·666	2·627
30	3·166	·648	3·814	3·927
40	3·812	·687	4·499	4·647
50	4·222	·707	4·929	5·055
80	4·773	·729	5·502	5·573
100	4·920	·735	5·655	5·720

(*b*) *Bodycentred lattice*: (i) **Tungsten.**—The elastic constants as measured by Bridgman (1924) are (in 10^{11} dyne/cm.^{2})

$$c_{11} = 51{\cdot}3 \qquad c_{12} = 20{\cdot}6 \qquad c_{44} = 15{\cdot}27$$

The temperature coefficients are not known but from the smallness of both γ and the thermal expansion, a very small change is expected at the low temperatures. The Debye characteristic temperature as calculated by Honnefelder (1933) is 384 and the reduced θ is 192. The frequencies and atomic heats are given in Tables VI (*a*) and (*b*) respectively.

TABLE VI (*a*)

Vibration frequencies of tungsten

	ν_1	ν_2	ν_3	ν_4	Reduced θ_D
Calculated from elastic constants cm.$^{-1}$	244	134	134	189	..
$\frac{h\nu}{k}$	351	192	192	271	192

TABLE VI (*b*)

Specific heats of tungsten cals./deg. gm. atom

Experimental data of Lange (1924) and *Zwikker* (1928 *from* 100–300)

Temperature °K.	Calculated c_v			Experimental c_v
	Optical Spectrum	Elastic spectrum	Total c_v	
26·01	·104	·127	·231	·213
32·3	·290	·201	·491	·431
38·8	·572	·279	·851	·750
46·7	·973	·363	1·34	1·21
54·7	1·395	·431	1·83	1·80
74·4	2·326	·545	2·87	2·87
78·3	2·495	·562	3·06	3·07
84·2	2·714	·583	3·30	3·33
91·1	2·945	·603	3·55	3·60
100	3·209	·624	3·83	3·77
200	4·559	·712	5·27	5·30
300	4·903	·730	5·63	5·87

(ii)–(iv) *Alkali metals.*—The quantity $c_{11} - c_{12}$ which determines ν_3 is a very small quantity for all these metals and is liable to be affected seriously by any approximations. We will show later that the present force model is not exactly valid in these cases. As before we have taken the value of ν_3 empirically in the II set of calculations and it will be seen that the empirical ν_3 is much larger than the theoretical value.

(ii) **Lithium.**—Amongst the metals of the simplest structure the specific heats of lithium show the most abnormal behaviour towards the Debye

function. The elastic constants have not been measured experimentally but Fuchs (1936 *b*) has calculated them theoretically for the absolute zero of temperature. His values are (in 10^{11} dyne/cm.^{2})

$$c_{11} = 1{\cdot}53 \times 10^{11} \qquad c_{12} = 1{\cdot}19 \times 10^{11} \qquad c_{44} = 1{\cdot}329 \times 10^{11}$$

The frequencies and the specific heats calculated from them are given in the Tables VII (*a*) and (*b*) respectively. The Debye characteristic temperature calculated by Bender (1939) is 333 and the reduced value 167.

TABLE VII (*a*)

Vibration frequencies of lithium

	ν_1	ν_2	ν_3	ν_4	Reduced θ_D
Calculated from elastic constants cm.$^{-1}$	300	212	76	300	..
$\frac{h\nu}{k}$	430	304	109	430	167
II set ν_3 empirical $\frac{h\nu}{k}$	,,	,,	218	,,	,,

TABLE VII (*b*)

Specific heats of lithium, cals./deg. gm. atom

Experimental data of Simon and Swain (1935)

Temperature °K.	Calculated c_v I set			Calculated c_v II set	Experiemntal c_v
	Optical frequencies	Elastic spectrum	Total c_v		
15	·055	·042	·097	·042	·045
20	·192	·092	·284	·095	·095
30	·555	·229	·784	·290	·273
40	·876	·355	1·23	·595	·573
50	1·173	·451	1·62	·979	·995
60	1·476	·520	2·00	1·41	1·42
80	2·085	·604	2·69	2·24	2·31
100	2·654	·650	3·30	2·97	3·03
120	3·128	·676	3·80	3·55	3·59
160	3·808	·706	4·51	4·36	4·34
200	4·225	·719	4·94	4·84	4·78
240	4·485	·726	5·21	5·14	5·09
260	4·585	·730	5·32	5·25	5·22
280	4·667	·731	5·40	5·34	5·31
300	4·731	·732	5·46	5·41	5·39

(iii) **Sodium.**—The elastic constants as measured by Bender (*l.c.*) at − 190° C. are (10^{11} dynes/cm.^{2})

$$c_{11} = {\cdot}945 \qquad c_{12} = {\cdot}779 \qquad c_{44} = {\cdot}618$$

Quimby and Seigel's measurements (1938) differ considerably from these and are at 80° K.

$$c_{11} = \cdot 608 \qquad c_{12} = \cdot 463 \qquad c_{44} = \cdot 593$$

The frequencies given in Table VIII (*a*) have been calculated from Bender's data. In the second (empirical) set of calculations ν_1 also has been slightly altered. The new value is very near the one given by the data of Quimby and Seigel. The characteristic frequency has been reduced from the one given by Bender.

TABLE VIII (*a*)

Vibration Frequencies of Sodium

	ν_1	ν_2	ν_3	ν_4	Reduced θ_D
Calculated from Bender's data cm.$^{-1}$	136	88	32	124	..
$\frac{h\nu}{k}$	195	126	46	178	92
II set ν_1 and ν_3 empirical $\frac{h\nu}{k}$ ..	160	,,	80	,,	,,

TABLE VIII (*b*)

Specific heats of sodium, cals./deg. gm. atom

Experimental data of Simon and Zeidler (1926)

Temperature °K.	Calculated c_v I set			Calculated c_v II set	Experimental c_v
	Optical frequencies	Elastic spectrum	Total c_v		
16·95	·888	·240	1·128	·604	·592
23·25	1·325	·379	1·70	1·27	1·21
26·17	1·527	·430	1·96	1·64	1·55
29·4	1·755	·478	2·23	1·95	1·93
34·6	2·121	·538	2·66	2·49	2·47
41·4	2·543	·622	3·17	3·10	3·09
49·5	3·012	·630	3·64	3·67	3·78
58·1	3·419	·659	4·08	4·13	4·24
117·6	4·628	·722	5·35	5·41	5·50

(iv) **Potassium.**—Bender's measurements (*l.c.*) for elastic constants are (10^{11} dynes/cm.^{2})

$$c_{11} = \cdot 459 \qquad c_{12} = \cdot 372 \qquad c_{44} = \cdot 263$$

The characteristic temperature as given in Table IX (*a*) has been reduced from Bender's calculations. The atomic heats are given in Table IX (*b*).

TABLE IX (*a*)

Vibration frequencies of potassium

	ν_1	ν_2	ν_3	ν_4	Reduced θ_n
Calculated from elastic data cm.$^{-1}$	78	48	20	69	..
$\frac{h\nu}{k}$	112	70	29	100	48
II set (ν_3 empirical) $\frac{h\nu}{k}$	,,	,,	58	,,	,,

TABLE IX (*b*)

Specific heats of potassium, cals./deg. gm. atom

Experimental data of Simon and Zeidler (l.c.)

Temperature °K.	Calculated c_v I set			Calculated c_v II set	Experimental c_v
	Optical frequencies	Elastic spectrum	Total c_v		
14·71	1·473	·461	1·93	1·31	1·23
17·30	1·822	·523	2·35	1·79	1·79
19·00	2·030	·553	2·58	2·08	2·09
22·83	2·487	·604	3·09	2·68	2·68
24·21	2·637	·617	3·25	2·88	2·89
31·05	3·274	·663	3·94	3·67	3·73
36·00	3·610	·683	4·29	4·08	4·15
47·2	4·162	·708	4·87	4·74	4·85
64·1	4·591	·724	5·32	5·24	5·30
71·8	4·718	·728	5·45	5·39	5·41
98·3	4·924	·735	5·66	5·63	5·72

6. *Discussion of the Results*

(*a*) *Face-centred lattice.*—Considering the approximations used in deriving the frequencies, the agreement between the calculated and experimental values of c_v must be regarded as fairly satisfactory. The small discrepancy at the low temperatures is always due to the uncertainty in the Debye function, while a slight difference at the high temperatures arises from the fact that low temperature elastic data have been used in computing the frequencies. The agreement generally improves in the II set of calculations where ν_3 has been empirically increased by about 15%. Since in any rigorous calculations all the frequencies are liable to be effected to some extent or the other, the above difference in ν_3 undoubtedly exaggerates the actual discrepancy that is likely to exist between the real frequencies and those given by our model. In order to investigate the effect of a more

general force field on the frequencies, we have also tried to calculate them for the case when $\psi \neq 0$ but is a small fraction with the same sign of δ, and have found that the magnitudes of the frequencies always increase slightly. It is, therefore, probable that a more exact force field will raise the frequencies to the required order. There is, however, one more element of uncertainty in the present calculations. The lowest frequency is very sensitive to the difference $c_{11} - c_{12}$. It has been seen in some non-metallic crystals (Durand, 1936) that the percentage increase in c_{11} at the low temperatures is far out of proportion to that of c_{12} which in some cases does not change at all above its room temperature value. If this is the case in the metallic crystals also, ν_3 will rise much above the value calculated here.

(*b*) *Body-centred lattice.*—The calculated and observed c_v agree very well in the case of tungsten, where the small discrepancy at low temperatures is due to the uncertain Debye function which is not a rigorous part of Raman's theory and also due to the use of the room temperature elastic data. In the case of alkali metals the agreement can only be reached by increasing ν_3 to about double its value. In the body-centred lattices this frequency depends only on $(c_{11} - c_{12})$ which is the difference of two nearly equal quantities in the case of alkali metals, and is liable to be greatly influenced by the uncertainties in the forces. Further the present model is hardly applicable to these metals. Fuch's calculations (*l.c.*) of the elastic constants $(c_{11} - c_{12})$ and c_{44} of metals show that they are determined by two factors, (i) the electrostatic (coulomb) cnergy of the lattice, (ii) the non-coulomb ion-ion interaction. The calculation of the first is not confined to neighbouring points of the lattice, while the latter apart from a very small Van der Waals' term is almost completely determined by the neighbours and next nearest neighbours. In the case of copper the contribution of the second term to $(c_{11} - c_{12})$ is about eight times that of the coulomb term, while that to c_{44} is $2\frac{1}{2}$ times that of the latter. Calculations on the other noble metals have not been made, but Fuch's work (1935) on their compressibilities leads us to expect an even greater contribution by the ion-ion interaction. If we include aluminium and lead also in the same category, it becomes obvious that for all the face-centred metals which have been studied here, very satisfactory values of force constants can be obtained by confining ourselves to the effects of neighbours and next neighbours only. In alkali metals the situation is exactly the reverse and the elastic constants are almost completely determined by the long range coulomb term so that it is quite incorrect to consider the effects of the neighbouring atoms only. Since the small quantity $(c_{11} - c_{12})$ is more likely to be influenced by any approximation, it is not surprising that our values of ν_3 are abnormally low.

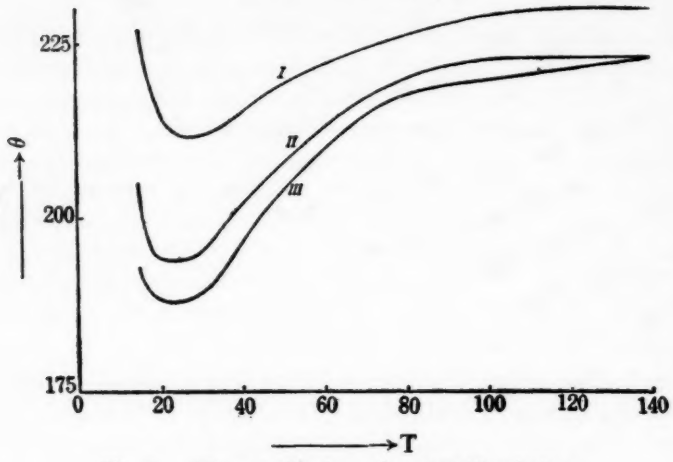

Fig. 3. θ/T curves for Ag under assumed anisotropy.
I $\frac{2C_{44}}{C_{11}-C_{12}}=\frac{4}{3}$. II $\frac{2C_{44}}{C_{11}-C_{12}}=2{\cdot}6$. III $\frac{2C_{44}}{C_{11}-C_{12}}=4$

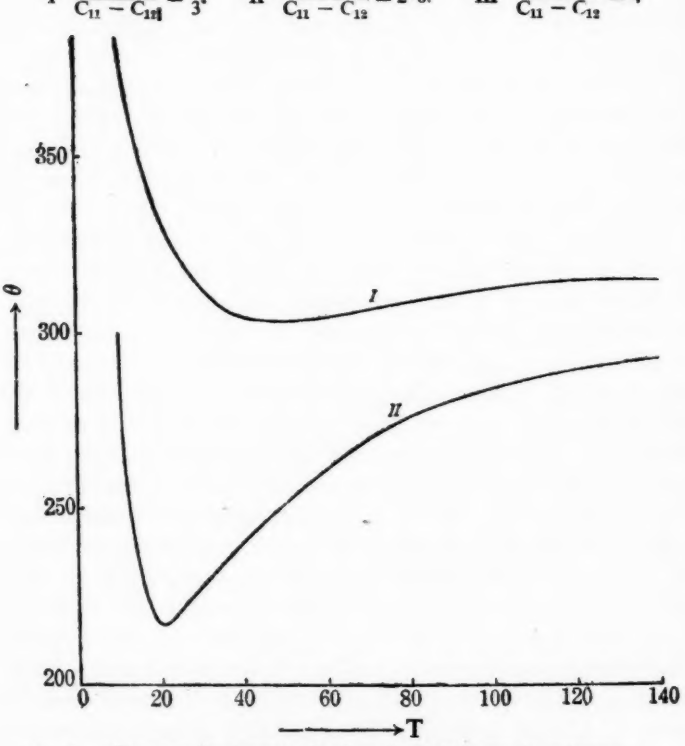

Fig. 4. θ/T curves for tungsten for hypothetical change in anisotropy.
I $\frac{2C_{44}}{C_{11}-C_{12}}=1$ (actual value) II $\frac{2C_{44}}{C_{11}-C_{12}}=4$

As a matter of fact Fuchs (1936 *b*) has himself remarked that the anisotropy, which for long waves is given by $\frac{2c_{44}}{c_{11}-c_{12}}$ is likely to be much less for shorter waves. The fact that on replacing ν_3 by an empirical value, the calculated c_v for all the alkali metals (particularly so far lithium and potassium) agrees well with the experimental data at all temperatures is an indication that the empirical value selected by us is the correct frequency for the mode in question.

7. *The Debye-Function as an Interpolation Formula*

It is usual to compare Debye's theory with the experimental data by calculating the characteristic temperature θ of the function for each observed value of c_v. If Debye's theory is correct, θ would be a constant independent of the temperature. With the exception of gold this is approximately so for all the face-centred metals at the high temperatures. At the low temperatures where Debye's theory should be rigorously valid, θ is not constant but varies with the temperature. According to Giaque and collaborator's data (*l.c.*) θ passes through a minimum at about $\theta/10$ and then rises again. The position of the minimum and its actual magnitude differs for different metals, and according to the present study seems to be closely related to the elastic anisotropy $\frac{2c_{44}}{c_{11}-c_{12}}$. The specific heats at low temperatures are almost entirely determined by the two lowest frequencies ν_2 and ν_4 which are given by

$$\nu_2 = \frac{1}{2\pi}\sqrt{\frac{(c_{11}-c_{12}+c_{44})\,a}{m}} \quad \nu_4 = \frac{1}{2\pi}\sqrt{\frac{4ac_{44}}{m}}.$$

For a perfectly isotropic substance $c_{11}-c_{12}=2c_{44}$ and the two frequencies are nearest together. For higher anisotropy ν_2 becomes smaller and causes an increase in the specific heat at the lower temperatures. In Fig. 3 we have plotted the θ/T curve for silver for the actual anisotropy (2·6) and have shown how the shape of the curve will change when the anisotropy is altered to $\frac{1}{3}$ and 4 which are very near the observed anisotropy of aluminium and lead respectively. All the other frequencies except ν_2 are supposed to be unaffected by this change. It is seen that the minimum is greater and shifts slightly towards the lower temperatures for large anisotropy—a fact fully borne out by Giaque's observations, who had ascribed this feature to the difference in the characteristic temperatures of each substance.

At higher temperatures the constant value of θ is only accidental. It is well known that the Nernst-Lindemann two frequency formula approximates to a Debye function at the high temperatures, and Debye (1912) ascribed the success of the former to this accidental feature. In the light of

the present work the success of the Debye function itself is the outcome of the particular dispositions of the Einstein frequencies. In gold where, due to the abnormally low value of c_{44} in comparison with the other constants, the frequency ν_4 has become very small compared to the higher frequencies the Debye formula completely breaks down.

In the body-centred metals the lowest frequency is given by $\frac{1}{2\pi}\sqrt{\frac{2(c_{11}-c_{12})}{m}}$. For perfect isotropy this becomes exactly equal to the next higher frequency ν_2. The two lowest frequencies never become identical in the face-centred metals so that the specific heats of isotropic bodies in the body-centred case yield a slightly different θ/T curve than is the case with the other crystal type. This seems to be the reason why the characteristic temperature of tungsten, which is a perfectly isotropic crystal, increases at low temperature. When the anisotropy is greater, ν_3 becomes very small, with the result that θ decreases with the fall of temperature, and we get a θ/T curve of the type given by lithium. This is shown clearly in Fig. 4 where we have plotted the θ/T curve for tungsten for the hypothetical case when the anisotropy becomes equal to 4, and all other frequencies except ν_3 remain unaltered in magnitudes. The curve II of this figure is to be contrasted with the curve III of Fig. 3 for the face-centred metals. The anisotropy is the same in the both cases but the lowest frequency in the face-centred case never becomes very low for any anisotropy whatsoever because of the presence of c_{44} in addition to $c_{11}-c_{12}$ in the frequency formula. The upper part of the curve III of Fig. 3, therefore, approximately becomes a straight line at moderately high temperatures while the curve II of Fig. 4 never shows this behaviour. It is not surprising, therefore, that the specific heats of most of the face-centred metals are approximately described by a Debye function at moderately high temperatures while the most conspicious cases of its failure come from the body-centred structures. It must be pointed out, however, that the above discussion is purely qualitative, since a change of anisotropy generally changes the other frequencies as well as the Debye characteristic temperature pertaining to the elastic spectrum.

In conclusion, the author wishes to record his grateful thanks to Professor Sir C. V. Raman, Kt., F.R.S., N.L., for his kind suggestions and guidance in the course of the work.

8. *Summary*

The specific heat data of the five face-centred (aluminium, silver, gold, copper and lead) and of the four body-centred metals (lithium, potassium,

sodium and tungsten), crystallising in the cubic system have been evaluated on the basis of the Raman dynamics of crystal lattices. The four discrete frequencies of atomic vibration in the crystal lattices indicated by the theory are evaluated in terms of the known elastic constants of the crystal, while the residual degrees of freedom not covered by these modes (which form one-eighth of the total number) are represented by a Debye function with a correspondingly reduced characteristic temperature. A fair agreement between the calculated values and experimental data is obtained. The agreement is greatly improved if the lowest of the four calculated frequencies is somewhat increased in most cases, a procedure which is justified by the fact that the calculations are based on a highly simplified form of the atomic force field involving only three force constants. It is also shown that the degree of accuracy with which the specific heat data of a metal can be represented by a single Debye function is largely accidental, and depends on the relationship between the frequencies of the four fundamental modes of vibration of the lattice.

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THE LOCALISATION THEORY IN SET-TOPOLOGY

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The earliest notion which could be described as the starting point of set-topology is Cantor's concept of the derived set D(X) of a set X of real numbers, defined as the set of points of X which are accumulation points thereof. This was generalised by Frechêt into the abstract topological notion of the *derived set* D(X) of a set X, defined as the set of all *limit-elements* of X. In the present-day treatments of set-topology, a greater prominence is generally given to the *closure function* $\overline{X} = X + D(X)$, introduced postulationally by Kuratowski. The connection between the *closure* and the *derivate* of a set X may be described by saying that in the topology defined by the closure-function, both the closure $\overline{X}$ and the derived set D(X) appear as *local* functions of X ; namely $\overline{X}$ is the set of points at which X is not locally *null*, while (assuming that the topology is T_1) D(X) is the set of points at which X is not locally *finite*. The idea of localisation of properties thus suggested has been treated in a general manner by Kuratowski in his *Topologie*, with a systematic calculus; a notable achievement of the calculus is the elegant proof that it gives of the theorem that *the points at which a set of the second category is* **locally** *of the second category constitute a closed domain.* (The corresponding theorem for metric spaces was originally stated and proved by Banach.)

In this paper, I review the localisation theory and study the properties of what I have called *compact* and *super-compact* ideals (or hereditary additive properties), as well as certain extensions P_α, P_S, P_N of an ideal P.

I. Let R be a topological T_1-space, B_R the boolean algebra of all its subsets. A property P of subsets of R is *hereditary* if $Y < X$ and $X \epsilon P$ imply $Y \epsilon P$; it is *additive*, if $X \epsilon P$ and $Y \epsilon P$ imply $X + Y \epsilon P$. Given any property P of subsets of R, it is convenient to denote also by P the family of all subsets possessing the property P. If P is a hereditary additive property, it is clear that the family P is a μ-ideal of B_R; conversely corresponding to any μ-ideal P of B_R we have a hereditary additive property P, *viz.*, the property of belonging to the ideal P. In particular if P is the zero ideal, *i.e.*, the ideal containing the null set only, the corresponding hereditary additive property is the property of being null; if P is the ideal 1, *i.e.*, the

whole of B_R, the corresponding property is the universal property of being a subset of R; and so on.

We say that a set X has the property P *locally* at a point x, if there exists a neighbourhood U_x of x, such that $U_x \cdot X \epsilon P$. The set of points at which X does *not* have the property P locally is denoted by P(X). Thus $x \epsilon P(X)$ means that for *every* neighbourhood U_x of x, $U_x \cdot X$ does not have the property P, or briefly is not a P. If P is a hereditary property it will be sufficient to restrict ourselves to *open* neighbourhoods; for if $U_x \cdot X \epsilon P$, $(\text{Int. } U_x) \cdot X < U_x \cdot X$ is also a P, and since Int. U_x is also neighbourhood, $(\text{Int. } U_x) \cdot X \epsilon P$ implies X is locally P at x.

We shall consider only hereditary additive properties P; we shall call P(X) the *local function* of the corresponding ideal P.

II. *General Properties of the local function* P(X).*

(*a*) If $X < Y$, $P(X) < P(Y)$.

For if p is not in P(Y), it has an open neighbourhood G_p such that $G_p \cdot Y \epsilon P$.

Then $G_p \cdot X < G_p \cdot Y$ is also a P. Hence p is not in P(X). Thus $\{P(Y)\}' < \{P(X)\}'$ or $P(X) < P(Y)$.

(*b*) If $P < Q$ (*i.e.*, if the *ideal* P is contained in the ideal Q), $P(X) > Q(X)$.

For if X is locally P at x, it must also be locally Q at x (since every P is also a Q). Hence $\{P(X)\}' < \{Q(X)\}'$ or $P(X) > Q(X)$.

(*c*) P(X) is a closed set contained in $\overline{X}$.

For $\overline{X}$ is the local function O(X) of the zero ideal. Since the ideal P contains the zero ideal, it follows from (*b*) that $P(X) < \overline{X}$. To shew that P(X) is closed, any point $p \epsilon \{P(X)\}'$ has an open neighbourhood G_p such that $G_p \cdot X \epsilon P$. It is clear that X is locally P at every point of G_p. Thus $G_p < \{P(X)\}'$, or $\{P(X)\}'$ is open. Hence P(X) is closed.

(*d*) $PP(X) < P(X)$.

For by (*c*) $PP(X) < \overline{P(X)} = P(X)$.

(*e*) $P(X + Y) = P(X) + P(Y)$.

From (*a*) it follows that $P(X + Y) > P(X) + P(Y)$. To prove the reverse inclusion, let p belong neither to P(X) nor to P(Y). Therefore it has open neighbourhoods U_p, V_p, so that $U_p \cdot X \epsilon P$, $V_p \cdot Y \epsilon P$. As P is here-

*All these properties with the exception of (*b*) and (*f*) will be found in Kuratowski's *Topologie*, pp. 29, 30.

ditary and additive $U_pV_p(X + Y) \epsilon P$. Since U_pV_p is an open neighbourhood of p, it follows that p does not belong to $P(X + Y)$. Hence $\{P(X)\}' \cdot \{P(Y)\}' < \{P(X + Y)\}'$ or $P(X + Y) < P(X) + P(Y)$. Hence the result.

(*f*) If P_3 is the intersection of the ideals P_1, P_2, $P_3(X) = P_1(X) + P_2(X)$.

For by (*b*) $P_3(X) > P_1(X) + P_2(X)$. To prove the reverse inclusion, we observe that if X is locally P_1 as well as locally P_2 at x, there must exist open neighbourhoods U_x, V_x of x, so that $U_x \cdot X \epsilon P_1$, $V_x \cdot X \epsilon P_2$. Hence U_xV_xX is a P_1 and also a P_2; that is, $U_xV_xX \epsilon P_3$ or X is locally P_3 at x. Hence if X is *not* locally P_3 at x, it is either not locally P_1 or not locally P_2 there; *i.e.*, $P_3(X) < P_1(X) + P_2(X)$. This proves that $P_3(X) = P_1(X) + P_2(X)$.

(*g*) $P(X)\{P(Y)\}' = P(XY')\{P(Y)\}' < P(XY')$.

This follows since $P(X) = P(XY) + P(XY')$ and $P(XY) < P(Y)$ by (*a*).

(*h*) If G is open $G \cdot P(X) = G \cdot P(GX) < P(GX)$.

For if $p \epsilon G \cdot P(X)$, and H any open neighbourhood of p, HG is also a neighbourhood, and therefore HGX is not a P. Hence $p \epsilon P(GX)$. Thus $G \cdot P(X) < P(GX) < P(X)$ by (*a*).

Hence $GP(X) < G \cdot P(GX) < GP(X)$, which proves (*h*).

The additive property of P has been used in proving (*e*), (*g*) only.

Hence the remaining properties are all valid if P is hereditary without being additive.

III. *The fundamental series of ideals and their local functions.*—It was already noticed that the closure function $\overline{X}$ is the local function of the zero ideal O. This is the lowest of a series of ideals, which we may call *numerical ideals*, and denote by I_ω; where for any ordinal $\omega \geqslant 0$, we denote by I_ω the ideal of all sets whose potency is less than $\aleph_\omega$. I_0 (which we may write simply I) is thus the ideal of *finite* sets, I_1 the ideal of sets which are either finite or enumerable and so on. O and $I (= I_0)$ are the basic ideals we have to consider; the local function O(X) is $\overline{X}$, while the local function I(X) is the *derived set* of X, defined as the set of all accumulation points of X.† From II (*c*) I(X) is a closed set contained in $\overline{X}$, and $\overline{X} = X + I(X)$. A set X is said to be:

† The point x is said to be an *accumulation point* of the set X, if every neighbourhood of x contains a point of X other than x. If the space is T_1, the accumulation points of X are identical with the points at which X is not locally finite.

(1) *discrete* if $I(X) = 0$;

(2) *isolated* if $X \cdot I(X) = 0$;

(3) *dense-in-itself* if $X < I(X)$;

(4) *scattered*, if it contains no dense-in-itself subset;

(5) *closed*, if $X = \overline{X}$, or equivalently $I(X) < X$.

The discrete sets form an ideal $>$ I, which we call d; it is easy to shew that its local function $d(X)$ is equal to $I(X)$ (for proof, see IV). At this stage it is necessary to make the additional hypothesis that *space is dense-in-itself*; in other words that $I(1) = 1$. It follows then that *every open set as well as evey dense set is dense in itself.* For if G is any open set, its complement F is closed, and $1 = I(1) = I(G) + I(F) = G + F$. Since $I(F) < F$, it follows that $I(G) > G$ or G is dense in itself. Again, if X is a dense set, $\overline{X} = 1$, or $X + I(X) = 1$, whence $I(X) + II(X) = I(1) = 1$. By II(d) $II(X) < I(X)$. Hence $I(X) = 1 > X$; so that X is dense in itself. It follows from this that *scattered sets are non-dense.* For if X is scattered, and $\overline{X}$ contains an open set G, then $G = G\overline{X} < \overline{GX}$ [II (h)], so that GX is dense in G. But it was shewn that G is dense-in-itself; hence in the relative topology in which G is taken as space, GX being dense must be dense-in-itself. This is a contradiction, as X being scattered cannot have a dense-in-itself subset GX. Hence X is non-dense. It follows from this that *the scattered sets form an ideal* (*which we may call* **s**) *containing the ideal* **d** *of discrete sets.* For it is clear in the first place that any subset of a scattered set must be scattered. To prove that the union $X_1 + X_2$ of two scattered sets X_1, X_2 is scattered, suppose that D is a dense-in-itself subset of $X_1 + X_2$. Then DX_1, DX_2 are scattered sets, as subsets of X_1, X_2. Taking D as the dense-in-itself space, DX_1 as scattered set, must be non-dense relatively to D; hence its relative complement, which is a subset of DX_2, must be dense in D, and therefore dense-in-itself. This contradicts the assumption that X_2 is scattered. This proves that the union of two scattered sets is scattered. We proceed now to evaluate the local function $s(X)$ of the ideal s of scattered sets.

Given any family of dense-in-themselves sets X, it is easy to see that their union ΣX must be dense-in-itself; for $\Sigma X >$ each X; hence $I(\Sigma X) >$ each $I(X) > X$. Hence $I(\Sigma X) > \Sigma X$, or ΣX is dense-in-itself. If now X is an arbitrary set, the union K(X) of all dense-in-themselves subsets of X must therefore be dense-in-itself; K(X) is thus the *maximal* dense-in-itself subset of X, or *the dense-in-itself kernel* of X. $X \cdot \{K(X)\}'$ must therefore be a scattered set, since it can have no dense-in-itself subset. We can now see that *the local function* $s(X)$ *of the ideal* **s** *of scattered sets is equal*

to the closure $\overline{K(X)}$ *of the dense-in-itself kernel* $K(X)$ *of* X. For if x be a point of $\overline{K(X)}$, and G *any* neighbourhood of x, $G \cdot K(X) \neq 0$, and is a relatively open subset of the dense-in-itself set K (X). Hence $G \cdot K(X)$ is dense-in-itself and therefore $G \cdot X > G \cdot K(X)$ is not scattered for any neighbourhood G of x. Hence X is not locally scattered at any point of $\overline{K(X)}$. On the other hand if x is any point not in $\overline{K(X)}$, it has a neighbourhood G disjoint with K (X), and $G \cdot X$ is scattered, since it is a subset of the scattered set $X \cdot \{K(X)\}'$. Thus X is locally scattered at every point not in $\overline{K(X)}$. This proves that $s(X) = \overline{K(X)}$. It follows from this, that if $X \cdot s(X) = 0$, X must be scattered. For,

$$0 = X \cdot s(X) = X \cdot \overline{K(X)} > X \cdot K(X) = K(X).$$

Hence $K(X) = 0$, and therefore X must be scattered.

The next ideal in the series is *the ideal N of non-dense sets* (which, as every scattered set is non-dense, contains the ideal s of scattered sets). A *non-dense set* is defined to be one whose closure is a boundary set, (or, alternatively, whose exterior is dense). It is obvious from the definition, that a subset of a non-dense set is non-dense. To shew that the non-dense sets form an ideal, we have to shew in addition that the union of two non-dense sets is non-dense. Let N_1, N_2 be two non-dense sets, and let $\overline{N}_1 + \overline{N}_2$ contain if possible a non-null open set G. Then

$$G = GN_1 + G\overline{N}_2.$$

Now $G\overline{N}_1$ is a non-dense set, which is also non-dense relative to G; hence its relative complement, which is a subset of $G\overline{N}_2$, would be dense in G, so that its closure would contain the open set G. This contradicts the non-density of N_2. Thus the existence of the ideal N of non-dense sets is established. We may shew that *the local function* $N(X)$ *of this ideal is equal to* $\overline{Int.\ X}$. To prove this, suppose that X is locally non-dense at x; then there is a neighbourhood G of x, such that GX, and therefore $\overline{GX}$ is non-dense. Hence $G\overline{X} < \overline{GX}$ must also be non-dense; hence G must be disjoint with Int. $\overline{X}$, and therefore with $\overline{Int.\ X}$. Thus x does not belong to $\overline{Int.\ X}$. Conversely if x does not belong to $\overline{Int.\ X}$, it has a neighbourhood G disjoint with Int. $\overline{X}$, so that $G\overline{X} = G$. (Boundary $\overline{X}$) is non-dense, and therefore $GX < G\overline{X}$ is non-dense. This establishes the form stated for the local function N (X).

Lastly, defining *a set of the first category* as the union of an enumerable family of non-dense sets, it follows at once that the sets of the first category constitute an ideal N_σ which contains N, and is its σ-extension. We shall see presently that N_σ is an example of the supercompact ideal; hence its

local function $N_\sigma(X)$ has the property $N_\sigma\{N_\sigma(X)\} = N_\sigma(X)$ (see V below). We can use this to shew that $N_\sigma(X)$ is *a closed domain*. For, since $N_\sigma > N > 0$, it follows (II (*b*)) that:

$$N_\sigma(X) < N(X) = \overline{\text{Int. } X} < \overline{X}.$$

Now $N_\sigma(X)$ is closed (II (*c*)); substituting $N_\sigma(X)$ for X in this, we have

$$N_\sigma N_\sigma(X) < \overline{\text{Int. } N_\sigma(X)} < N_\sigma(X).$$

Since $N_\sigma N_\sigma(X) = N_\sigma(X)$, it follows that $N_\sigma(X) = \overline{\text{Int. } N_\sigma(X)}$ is a closed domain. We may set down for reference, the six fundamental ideals and their local functions; *viz.*, $0 < I < d < s < N < N_\sigma$.

0	I	*d*	*s*	N	N_σ
The zero-ideal comprising the null-set only $0(X) = \overline{X}$	The ideal of finite sets $I(X)$ = derived set of X	The ideal of discrete sets $d(X) = I(X)$	The ideal of scattered sets $s(X) = \overline{K(X)}$ $K(X)$=dense-in-itself kernel of X	The ideal of non-dense sets $N(X) = \overline{\text{Int. } X}$	The ideal of sets of the 1st category $N_\sigma(X)$= closed domain < $N(X)$

IV. *Compact ideals.*—If P is any ideal and $X \epsilon P$, it is clear that $P(X) = 0$; but the converse '$P(X) = 0$ implies $X \epsilon P$' is not generally true. If $P(X) = 0$ implies $X \epsilon P$, we shall cell P a *compact* ideal.

Among the six fundamental ideals listed above, it is easy to see that all are compact with the exception of I, the ideal of finite sets. It is also easy to see that I will be compact if and only if the given topological space is *compact*, in which case the ideal *d* will coincide with I. In fact *d* could be described as the minimal compact extension of I. A similar extension can be carried out for a general non-compact ideal P as follows. Suppose Q is any compact ideal containing P; then $Q(X) = 0$ should imply $X \epsilon Q$. But as $Q > P$, $Q(X) < P(X)$ (II (*b*)). Hence $P(X) = 0$ implies $Q(X) = 0$. Hence Q should contain all sets X such that $P(X) = 0$. But the sets X such that $P(X) = 0$ themselves constitute an ideal (by II (*a*) and (*e*)), which we may call P_d. We shall shew that P_d is compact, so that it is the *minimal compact extension* of P. We may prove this by shewing that the local function $P_d(X)$ is equal to $P(X)$. Suppose that X is locally P_d at x; then there is a neighbourhood G of x, such that $GX \epsilon P_d$, that is, such that $P(GX) = 0$. It follows that x is not in $P(GX)$, and therefore GX is locally P at x; hence there is a neighbourhood G' of x, so that $G'GX \epsilon P$. As G'G is itself a neighbourhood of x, this shews that X is locally P at x. Hence $\{P_d(X)\}' < \{P(X)\}'$, or $P_d(X) > P(X)$. But $P_d > P$, so that by II (*b*) $P_d(X) < P(X)$. Hence $P_d(X) = P(X)$. Hence $P_d(X) = 0$ is equivalent to

$P(X) = 0$ which implies by definition that $X \epsilon P_d$. Thus P_d is compact and is the minimal compact extension of P.

To explain the significance of this result, we observe that an ideal P determines not only a local function $P(X)$ which is the analogue of *the derived set*, but also a closure function $X + P(X)$; that $X + P(X)$ satisfies all Kuratowski's postulates for the closure function follows from II (*d*) and (*e*). Thus each ideal P determines, through the closure function $X + P(X)$, a topology on the space which we may call the P-topology; since $X + P(X) < \overline{X}$, the P-topology is *weaker* than the original topology, so that open (or closed) sets continue to be open (or closed) in the P-topology. Also the P-topology is T_1, and would be Hausdorff if the original topology is Hausdorff. The ideal P_d is now seen to consist of the family of *discrete sets* of the P-topology. Thus the extension of P to P_d is fully parallel to the extension of the ideal of finite sets to the ideal of discrete sets.

V. *Supercompact ideals.*—We call an ideal P *supercompact*, if $XP(X) = 0$ implies $X \epsilon P$. This is a stronger implication than '$P(X) = 0$ implies $X \epsilon P$'; for if $XP(X) = 0$ implies $X \epsilon P$, then, since $P(X) = 0$ implies $XP(X) = 0$, it would follow that $P(X) = 0$ implies $X \epsilon P$. Thus a supercompact ideal is necessarily compact, but the converse is not true. For example, the ideal *d* of discrete sets is compact but not obviously supercompact. The zero ideal is compact and supercompact. The ideal *s* of scattered sets is supercompact, since it was shewn in III that $Xs(X) = 0$ implies that X is scattered. The ideal N of non-dense sets is supercompact, since $N(X) = \overline{\text{Int. } X} = 0$ implies Int. $\overline{X} = 0$ or X is non-dense. It will be shewn presently that N_σ is supercompact. The ideal 1 consisting of all sets of space, is compact and supercompact since its local function $1(X)$ is identically zero.

Any one of the following is a necessary and sufficient condition for the ideal P to be supercompact:

(1) $XP(X) = 0$ implies $P(X) = 0$;

(2) X is locally P at every one of its points implies $X \epsilon P$;

(3) For every set X, $X \cdot \{P(X)\}' \epsilon P$,

(4) If X admits a relatively open covering by P-sets, $X \epsilon P$.

(1) and (2) only paraphrase the definition. To prove (3), we observe that if P is supercompact and $Y = X \cdot \{P(X)\}'$, then

$$Y \cdot P(Y) = X \cdot \{P(X)\}' \cdot P\{X \cdot (P(X)'\} < X \cdot \{P(X)\}' \cdot P(X) = 0.$$

Hence $Y = X \cdot \{P(X)\}' \epsilon P$. Conversely if for all X, $X \cdot \{P(X)\}' \epsilon P$, then $Y \cdot P(Y) = 0$ implies $Y = Y\{P(Y) + [P(Y)]'\} = Y\{P(Y)\}' \epsilon P$. Hence P is

supercompact. Lastly to prove (4), we have only to observe that X admits a relatively open covering by P-sets, if and only if it is locally P at every one of its points.

We have also the important result that *if P be supercompact* $PP(X) = P(X)$. For if P be supercompact, it follows from (3) that $P\left(X\{P(X)\}'\right) = 0$. By II (g), $P(X)\cdot[PP(X)]' < P\{X\cdot(P(X))'\} = 0$. Hence $P(X) < PP(X)$. But by II (d) $PP(X) < P(X)$. Hence the result.

Following a theorem of Banach, we will now shew that,

Any numerical extension of the ideal N is supercompact.

The proof is substantially the same for the general numerical extension, as for the σ-extension. Let N_k be any numerical extension of N (*i.e.*, the sets of N_k are unions of $\aleph_k$ non-dense sets; k being any ordinal $\geqslant 0$). Let S be any set admitting a covering by relatively open subsets X_α belonging to N_k. We suppose the sets (X_α) to be well-ordered, so that the suffix α runs through the range $1 \leqslant \alpha < \gamma$. Suppose now we have a well-ordered system G_α of non-null disjoint open sets such that (1) $SG_\alpha \epsilon N_k$ for all α, and (2) the system S_α is saturated. We can now write

$$S = \Sigma_\alpha S G_\alpha + (S - \Sigma_\alpha G_\alpha).$$

The theorem is proved if we shew that (1) $\Sigma_\alpha S G_\alpha \epsilon N_k$ and (2) $S - \Sigma_\alpha G_\alpha \epsilon N$. To prove (1) write

$$SG_\alpha = \Sigma_\beta N_\beta^\alpha \quad 1 \leqslant \beta \leqslant \Omega_k; \quad N_\beta^\alpha \epsilon N.$$

This is possible since $SG_\alpha \epsilon N_k$. Write now

$$\Sigma_\alpha N_\beta^\alpha = N_\beta; \quad \Sigma_\alpha SG_\alpha = \Sigma_\beta N_\beta \cdot (1 \leqslant \beta \leqslant \Omega_k);$$

where Ω_k is the initial ordinal of the class $\aleph_k$. Now any N_β^α is relatively open in N_β, since, the G_α's being mutually disjoint, $N_\beta^\alpha = G_\alpha \cdot N_\beta$. Thus each N_β admits a covering by relatively open non-dense subsets, and is therefore non-dense (since the ideal N is supercompact). Therefore $\Sigma SG_\alpha = \Sigma N_\beta$ is a set of N_k. To prove (2), we have to use the assumed saturation of the system G_α. Denote by F the closed set $(\Sigma G_d)'$. If F has an interior H, then since the system G_α is saturated, SH does not belong to N_k; in particular, $S\cdot H \neq 0$, so that H intersects an X, say $X_t \cdot HX_t$ being a subset of X_t, belongs to N_k. We can find an open set $G < H$ such that $SG = HX_t$; namely take G as the part of H contained in Ext. $SX_t' = \overline{SX_t'}$. Since X_t is relatively open in S, Ext. $SX_t' \cdot S = X_t$. Hence $SG = HX_t$. We have therefore arrived at the contradiction that there exists a non-null open set

G, disjoint with all the G_α's, so that $S \cdot G$ belongs to N_λ. Thus the closed set F can have no interior, and must therefore be non-dense. Hence, $S - \Sigma G_\alpha$, as a subset of F must also be non-dense.

VI. *The supercompact ideal P_s.*—We have constructed the minimal compact extension P_d (corresponding to the ideal of P-discrete sets) of an arbitrary ideal P. We will now follow the analogy further, and construct a supercompact extension P_s of P, corresponding to the ideal of P-scattered sets. It is essential for this extension to assume that space is P-dense-in-itself, that is, that $P(1) = 1$.

A set X is *P-dense-in-itself* if $X < P(X)$. It is clear that the union of any family of P-dense-in-themselves sets must be P-dense-in-itself. Hence if X be any set, the union $K_p(X)$ of all P-dense-in-themselves subsets of X, is the maximal P-dense-in-itself subset of X, and may be called the P-kernel of X.

Any open set of the P-topology (and therefore also, any open set) is P-dense-in-itself. For if G is open in the P-topology, its complement F is closed, so that $P(F) < F$. Hence

$$G + F = 1 = P(1) = P(G) + P(F).$$

Since $P(F) < F$, it follows that $P(G) > G$, or G is P-dense-in-itself.

Again any dense set of the P-topology is P-dense-in-itself.

For if X is dense in the P-topology, $X + P(X) = 1$; hence $P(X) + PP(X) = P(1) = 1$. But by II (*d*), $PP(X) < P(X)$. Hence $P(X) = 1 > X$, so that X is P-dense-in-itself.

A set may be said to be *P-scattered* if it contains no P-dense-in-itself subset. It follows in particular, that if we remove from a set X, its P-kernel $K_p(X)$, what remains must be P-scattered. *Any P-scattered set is P-non-dense.* For let X be P-scattered, and let its P-closure $X + P(X)$ contain a P-open set G. Then $G = G$. P-closure of $X <$ P-closure of GX. Hence GX is dense in G (in the P-topology). Consider the relative P-topology in which G is taken as space; the condition that space is dense-in-itself is satisfied in this topology, since as a P-open set is P-dense-in-itself. GX being dense in this space must be P-dense-in-itself. This contradicts the assumption that X, as scattered set contains no P-dense-in-itself subset. Hence the theorem.

It is clear that any subset of a P-scattered set is P-scattered. Also *the union $X_1 + X_2$ of two P-scattered sets must be P-scattered.* For if it contains a P-dense-in-itself subset D, then DX_1 must be non-dense in the relative P-topology of D, hence its relative complement, which is a subset of DX_2,

must be dense in D, and therefore P-dense-in-itself, contradicting the assumption that X_2 is P-scattered. Thus *the P-scattered sets form an ideal P_s which contains P_d.*

We can now shew that *the local function $P_s(X)$ of the ideal P_s, is equal to $\overline{K_p(X)}$, where $K_p(X)$ is the P-kernel of X.* For if x is a point belonging to the kernel $\overline{K_p(X)}$, and G is any open neighbourhood of x, $GX > G \cdot K_p(X) \neq 0$. Now G is open and therefore open in the P-topology also. Considering $K_p(X)$ as the dense-in-itself of its relative P-topology, $G \cdot K_p(X)$ as relatively open subset of $K_p(X)$ is P-dense-in-itself. Thus GX is not P-scattered; or X is not locally P-scattered at x. On the other hand if x is not in $K_p(X)$, it has an open neighbourhood G disjoint with $K_p(X)$; then GX is a subset of the P-scattered set $X \cdot \{K_p(X)\}'$, and therefore P-scattered. Thus X is locally P-scattered at x. This proves that $P_s(X) = \overline{K_p(X)}$.

We can see finally that P_s is supercompact, so that it is a super-compact extension of P or P_d. For if $XP_s(X) = 0$, then

$$K_p(X) = XK_p(X) < X \cdot \overline{K_p(X)} = X \cdot P_s(X) = 0;$$

hence X is P-scattered and belongs to P_s, since its P-kernel is null.

VII. *The supercompact ideal P_N.*—The non-dense sets of the P-topology, form an ideal P_N which contains the ideal P_s of the P-scattered sets. This does not require a special proof; for, so long as we are handling only a single topology, *e.g.*, the P-topology, general theorems like 'Non-dense sets constitute an ideal' will continue to be true. It is only in the matter of the local functions that we have to exercise care, since there is a mix-up of two topologies (the original topology of the space enters through the neighbourhoods used in the definition of the local function).

We next proceed to shew that *the local function $P_N(X)$ of P_N is equal to*

$$\text{closure. } \text{Int}_p \cdot \text{closure}_p(X) = \overline{\text{Int}_p\left(X + P(X)\right)}:$$

(where 'Int_p' means that the Interior function is to be interpreted in the sense of the P-topology). To prove this, let X be locally P-non-dense at x; then there is an open neighbourhood G of x, so that GX is P-non-dense, and therefore also $\text{closure}_p(GX)$ is P-non-dense. Now G is an open set of the original topology, and therefore an open set of the P-topology; hence we can use the formula $G\overline{X} < \overline{GX}$; hence

$$G \cdot \text{closure}_p(X) < \text{closure}_p(GX),$$

and is therefore P-non-dense. Hence G must be disjoint with $\text{Int}_p \text{closure}_p(X)$; since G is an open set of the original topology, it follows that x does not belong to $\text{closure} \cdot \text{Int}_p \text{closure}_p(X) = \overline{\text{Int}_p(X + P(X))}$. Conversely, if x

does not belong to $\overline{\text{Int.}_\rho (X + P(X))}$, it follows that it has an open neighbourhood G disjoint with $\text{Int}_\rho (X + P(X))$. Hence $GX < G\left(X + P(X)\right) = G$. $\text{Boundary}_\rho \left(X + P(X)\right)$. Since the boundary of a closed set is non-dense, it follows that the last term, and hence GX is P-non-dense. Hence X is locally P-non-dense at x. This establishes the form stated for the local function $P_N(X)$.

Finally, we can shew that the ideal P_N is supercompact, and therefore a supercompact extension of the supercompact ideal P_s. For, if $X \cdot P_N(X) = 0$, $X \cdot \text{Int.}_\rho \cdot \{\text{closure}_\rho X\} < X \cdot P_N(X)$ is also null. Since $X < \text{closure}_\rho (X)$, and since X is disjoint with $\text{Int.}_\rho \cdot \{\text{closure}_\rho (X)\}$, it follows that $X < \text{Boundary}_\rho \{\text{closure}_\rho X\}$. Since the boundary of a closed set is non-dense, it follows that X is P-non-dense, and therefore belongs to P_N. Thus P_N is supercompact.

VIII. *The ideal* $P_{N\sigma}$.—The sets of the first category in the P-topology form the σ-extension of the ideal P_N. We would not however be able to say that this extension is supercompact; for an examination of the proof of the supercompactness of numerical extensions of N will shew that the non-dense character enters essentially in the proof. For a similar reason, we cannot assert the supercompactness of a numerical extension of any supercompact ideal.

SOME APPLICATIONS OF RAMANUJAN'S TRIGONOMETRICAL SUM $C_m(n)$

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THE object of this paper is to exhibit the application of Ramanujan's trigonometrical sum[1] to two arithmetical theories, the theory of Relative partitions (mod m) of Von Sterneck[2] and the theory of the class division of the integers mod m of Dr. R. Vaidyanathaswamy.[3]

If $n \equiv e_1 + e_2 \ldots$ (mod m), n is said to be relatively partitioned (mod m). Von Sterneck obtained explicit expressions for various numerical functions in this theory. He showed that these functions assume neat forms when expressed in terms of a certain arithmetic function $f(n, m)$ of two arguments. This function of Von Sterneck was recently proved by me[4] to be identical with Ramanujan's trigonometrical sum $C_m(n)$. Using this fact I prove all of Von Sterneck's results by a method which besides being easy and direct shows clearly the fundamental nature of the trigonometrical sum in this theory.

Dr. R. Vaidyanathaswamy studied a class division of the integers mod m, in which these integers are divided into a certain number of classes C_1, $C_2 \ldots$ according to their g.c.d. with m. He proved the remarkable theorem that these classes combine by addition, *i.e.*, that they form elements of a linear associative algebra with the scheme

$$C_i C_j = \sum_k \gamma_{ij}^k C_k$$

where $C_i C_j$ means the set of numbers, obtained by adding each number of C_i to each number of C_j. It is shown here that γ_{ij}^k could be expressed in terms of Ramanujan's sum. In fact

$$\gamma_{ij}^k = \frac{1}{m} \sum_{\delta/m} C_{\frac{m}{i}}(\delta)\, C_{\frac{m}{j}}(\delta)\, C_{\frac{m}{\delta}}(t_k)$$

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* I am indebted to Dr. R. Vaidyanathaswamy for his help in the preparation of this paper.

[1] Collected papers of S. Ramanujan (Cambridge), 1927, p. 179.

[2] Bachmann, *Niedere Zahlentheorie*, Bd. 2, 222–41.

[3] *Proc. Ind. Acad. Sci.*, 1937, **5**, 63–75.

[4] *Journal of the Madras University*, 1943, **15**, 1–9.

These references will hereafter be quoted by the numbers given above.

I prove more generally that

THEOREM.—$C_1^{a_1} C_2^{a_2} \ldots = \sum_k A_k C_k$ where

$$A_k = \frac{1}{m} \sum_{\delta | m} C_{\frac{m}{t_1}}^{a_1}(\delta) C_{\frac{m}{t_2}}^{a_2}(\delta) \ldots\ldots C_{\frac{m}{\delta}}(t_k).$$

I find also an expression for a certain numerical function connected with the theory of relative partitions (mod m), the set of integers used being those less than and prime to m. I prove also the interesting results.

(1) *If* m *is even then every odd number is the sum mod* m *of three and every even number is the sum mod* m *of two numbers less than and prime to* m.

(2) *If* m *is odd then every number is the sum mod* m *of two numbers less than and prime to* m.

2. Ramanujan's sum is

$$C_m(n) = \sum_k e^{2\pi i k n/m} = C_m(-n)$$

where k runs through all the integers less than and prime to m. Hardy[5] proved that

$$C_m(n) \cdot C_{m'}(n) = C_{mm'}(n) \qquad (m, m') = 1$$

and

$$C_m(n) = \sum \mu\left(\frac{m}{\delta}\right) \delta$$

the summation being over the common divisors of m and n and $\mu(n)$ is the Moebius function[6] we shall now prove the

Lemma A*.—$C_m(n) = \mu\left(\frac{m}{d}\right) \frac{\phi(m)}{\phi\left(\frac{m}{d}\right)}$ $\qquad d = (m, n)$

where $\phi(n)$ is Euler's function.

Proof.—$C_m(n) = \sum_{\delta | d} \mu\left(\frac{m}{\delta}\right) \delta = \sum_{\delta | d} \mu\left(\frac{m}{d} \cdot \delta\right) \frac{d}{\delta}$.

We might sum, naturally, for those divisors d_1 of d which are prime to $\frac{m}{d}$, for otherwise $\mu\left(\frac{m}{d} \cdot \delta\right)$ vanishes. Thus

$$C_m(n) = d \sum_{d_1} \mu\left(\frac{m}{d}\right) \mu(d_1)\, d_1^{-1}$$

$$= d\, \mu\left(\frac{m}{d}\right) \sum_{d_1} \mu(d_1)\, d_1^{-1}$$

which is the right-hand side of the lemma.

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[5] *Proc. Camb. Phil. Soc.*, 1921, 263–71.

[6] Hardy and Wright, *Introduction to the Theory of Numbers*, p. 231.

* There is another proof in my paper, Ref. 4. See also Ö. Holder, *Prace. Matematyzno Fizycyn*, 1936, 13-23.

Corollary.—$C_m(n)$ depends on n only through its g.c.d. with m so that

$$C_m(n) = C_m(d).$$

Lemma B.—If f(m, r) *and* ϕ(m, r) *be two arithmetic functions possessing the modulus* m *and if*

$$\sum_{k=0}^{m-1} f(m,k)\,\rho^{kr} = \phi(m,r) \qquad \rho = e^{\frac{2\pi i}{m}}$$

then

$$\sum_{k=0}^{m-1} \phi(m,k)\,\rho^{-kr} = m f(m,r)$$

Proof.—

$$\sum_{\lambda=0}^{m-1} \phi(m,\lambda)\,\rho^{-\lambda r} = \sum_{\lambda=0}^{m-1}\sum_{k=0}^{m-1} f(m,k)\,\rho^{(k-r)\lambda}$$

$$= \sum_{k=0}^{m-1} f(m,k) \sum_{\lambda=0}^{m-1} \rho^{(k-r)\lambda}$$

The inner sum is zero except when $k = r$ when its value is m.

Lemma C.—If ϕ(m, r) *depends on* r *only through its g.c.d. with* m *then so does* f(m, r) *and then each of them can be expressed in terms of the other and Ramanujan's sum.*

Proof.— For if $\phi(m,r) = \phi(m,\delta) \qquad \delta = (m,r)$

then

$$\sum_{r=0}^{m-1} \phi(m,r)\,\rho^{-rk} = \sum_{d/m} \phi(m,d) \sum_{t} \rho^{-tk}$$

t running through all the integers mod m having with m a g.c.d. equal to d and

$$\sum_{t} \rho^{-tk} = C_{\frac{m}{d}}(k)$$

so that

$$m f(m,k) = \sum_{\delta/m} \phi(m,\delta)\, C_{\frac{m}{\delta}}(k)$$

$$\phi(m,k) = \sum_{\delta/m} f(m,\delta)\, C_{\frac{m}{\delta}}(k).$$

3. We shall now prove Von Sterneck's results by using the above lemmas.

THEOREM I. $$C_m(n) = \sum_{k=0}^{m-1} (-1)^k (n)_k^{(0)} = \sum_{\nu} (-1)^{\nu}$$

where $(n)_k^{(0)}$ *is the number of ways of expressing* n *as the sum mod* m *of* k *different elements of the set* 1, 2, 3....(m − 1) *and* ν *is the number of parts in a relative partition of* n *mod* m *into distinct parts not including zero.*

Proof.—If $\rho = e^{\frac{2\pi i}{m}}$ then

$$(1-\rho^r)(1-\rho^{2r})\ldots(1-\rho^{(m-1)r}) = \sum_{k=0}^{m-1} f(m,k)\,\rho^{rk}$$

where

$$f(m,k) = \sum_{t=0}^{m-1} (-1)^t (k)_t^{(0)}$$

But $(1-\rho^r)(1-\rho^{2r})\ldots(1-\rho^{(m-1)r}) = 0 \quad (m, r) > 1$
$= m \quad (m, r) = 1$

so that using lemma (*c*) we have

$$m f(m, k) = \sum_r m \rho^{-rk} \qquad (r, m) = 1 \quad 1 \leqslant r < m$$
$$= m C_m(k).$$

This is a direct and simple proof of the identity of Ramanujan's sum and Von Sterneck's function.

THEOREM 2.—

$$A(m, n) = \sum_{t=0}^{m-1} (n)_t^{(0)} = \frac{1}{2m} \Sigma 2^{m/\delta} C_\delta(n)$$

summation being for all odd divisors of m.

Proof.—It is easy to see that

$$\sum_{k=0}^{m-1} A(m, k) \rho^{kr} = \prod_{\lambda=1}^{m-1} (1 + \rho^{\lambda r}) = \tfrac{1}{2} \phi(m, r)$$

where $\phi(m, r) = \prod_{\lambda=1}^{m} (1 + \rho^{\lambda r})$.

The value of $\phi(m, r)$ depends on r only through its g.c.d. with m so that using lemma C we have

$$m A(m, n) = \tfrac{1}{2} \sum_{\delta | m} \phi(m, \delta) C_{\frac{m}{\delta}}(n).$$

But $\phi\left(m, \frac{m}{\delta}\right) = \left\{\left[1 + e\left(\frac{1}{\delta}\right)\right]\left[1 + e\left(\frac{2}{\delta}\right)\right]\ldots\left[1 + e\left(\frac{\delta}{\delta}\right)\right]\right\}^{\frac{m}{\delta}}$

where $e(x) = e^{2\pi i x}$.

Since $\frac{\sin m\theta}{\sin \theta} = 2^{m-1} \sin(\theta + \beta)\ldots\sin(\theta + \overline{m-1}\beta)$ where $\beta = \frac{\pi}{m}$

we see that, by putting $\theta = \frac{\pi}{2}$.

$$\left[1 + e\left(\frac{1}{\delta}\right)\right]\ldots\left[1 + e\left(\frac{\delta - 1}{\delta}\right)\right] = \sin\frac{\delta\pi}{2} \times (-1)^{\frac{\delta-1}{2}}.$$

Substituting this value we have the required result.

THEOREM 3.—*If* $(n)_k$ *denotes the number of ways of expressing* n *as the sum* (*mod* m) *of* k *integers of the set* 0, 1, 2....m − 1 *repetitions being allowed then*

$$[n]_k = \frac{1}{m} \sum_{\delta | m} \binom{\frac{m+k}{\delta} - 1}{\frac{k}{\delta}} C_\delta(n)$$

where $\binom{m}{n}$ *is the usual coefficient which vanishes if* n *or* m *is non integral.*

Proof.—It is easily seen that if $n \leqslant m$ and

$$A_a(r) = \sum_{k=0}^{m-1} [k]_a \rho^{kr} \qquad \rho = e^{\frac{2\pi i}{m}}$$

then $A_a(r)$ is the coefficient of x^a in the expansion of $[(1 - x\rho^r)(1 - x\rho^{2r}) \ldots (1 - x\rho^{mr})]^{-1}$ as a power series in x. But $(1 - x\rho^r) \ldots (1 - x\rho^{mr}) = (1 - x^{m/\delta})^{\delta}$ where $\delta = (m, r)$ so that $A_a(r)$ is the coefficient of x^a in the binomial expansion of $(1 - x^{m/\delta})^{-\delta}$

$$\therefore \quad A_a(r) = 0 \qquad \text{if } m/\delta \text{ does not divide } a$$

$$= (-1)^{\lambda} \binom{-\delta}{\lambda} \text{ when } \lambda = \frac{a\delta}{m}.$$

Thus $A_k(r) = \sum_{n=0}^{m-1} [n]_k \rho^{nr}$ and by lemma C we have the result.

THEOREM 4.—*If* $(n)_k$ *denotes the number of ways of expressing* n *as the sum* (*mod* m) *of* k *distinct integers of the set* 0, 1, ... m − 1 *then*

$$(n)_k = \frac{(-1)^k}{m} \sum_{\delta/m} (-1)^{k/\delta} \binom{m/\delta}{k/\delta} C_\delta(n)$$

Proof.—As in the previous theorem we see easily that $B_a(r) = \sum_{k=0}^{m-1} (k)_a \rho^{kr}$ is the coefficient of x^a in the expansion of $(1 + x\rho^r)(1 + x\rho^{2r}) \ldots (1 + x\rho^{mr})$. But $(1 - x\rho^r)(1 - x\rho^{2r}) \ldots (1 - x\rho^{mr}) = (1 - x^{m/\delta})^{\delta}$.

$$\therefore \quad B_a(r) = 0 \text{ if } m/\delta \text{ does not divide } a.$$

$$= (-1)^{\lambda} \binom{\delta}{\lambda} \times (-1)^{m\lambda/\delta} \text{ when } \lambda = \frac{a\delta}{m}.$$

$$= (-1)^{\frac{m\lambda}{\delta} + \lambda} \binom{\delta}{\lambda}$$

$$\therefore \quad B_k(r) = \sum_{n=0}^{m-1} (n)_k \rho^{nr}.$$

By lemma C we have the theorem.

4. We now proceed to the class division of the integers mod m. Let $t_1 (= 1), t_2, \ldots t_\lambda (= m)$ $[\lambda = d(m)]$ the number of divisors of m be the distinct divisors of m. Dr. R. Vaidyanathaswamy[3] divides the integers $1, 2 \ldots m$ into λ classes $C_1, C_2, \ldots C_\lambda$ in such a way that C_r contains those integers mod m which have with m a g.c.d. equal to t_r. Thus the number of elements in any set C_r is $\phi\left(\frac{m}{t_r}\right)$. These classes combine among themselves by means of addition. Let C_r consist of the integers $\beta_{1r}, \beta_{2r}, \ldots \beta_{g_r r}$ where $g_r = \phi\left(\frac{m}{t_r}\right)$. We shall prove the following :

THEOREM 5.

$$C_i C_j = \sum_k \gamma_{ij}^k C_k \text{ where}$$

$$\gamma_{ij}^k = \frac{1}{m} \sum_{\delta | m} C_{\frac{m}{t_i}}(\delta)\, C_{\frac{m}{t_j}}(\delta)\, C_{\frac{m}{\delta}}(t_k).$$

Proof.—If $\rho = e^{\frac{2\pi i}{m}}$ and

$$\left(\rho^{r\beta_{i1}} + \rho^{r\beta_{i2}} + \ldots\ldots \rho^{\gamma\beta g_{ij}}\right)\left(\rho^{r\beta_{j1}} + \rho^{r\beta_{j2}} + \ldots\ldots + \rho^{r\beta g_{jJ}}\right)$$
$$= \sum_{n=0}^{m-1} f(m, n)\, \rho^{nr}$$

then $f(m, n)$ is the number of ways of expressing n as the sum (mod m) of two numbers one from each of the sets C_i and C_j.

It is easy to see that $\sum \rho^{\alpha r}$ where α runs through all the elements of the set C_k has the value $C_{\frac{m}{t_k}}(r)$. Thus

$$\sum_{n=0}^{m-1} f(m, n)\, \rho^{nr} = C_{\frac{m}{t_i}}(r)\, C_{\frac{m}{t_j}}(r).$$

By lemma C we have the result.

THEOREM 6.

$$C_1^{\alpha_1} C_2^{\alpha_2} \ldots\ldots = \sum_k A_k C_k \quad \text{where}$$

$$A_k = \frac{1}{m} \sum C_{\frac{m}{t_i}}^{\alpha_1}(\delta) \ldots\ldots C_{\frac{m}{\delta}}(t_k).$$

Proof.—If $f(m, n)$ represents the number of ways of expressing n as the sum (mod m) of α_1 numbers of the set C_1, α_2 numbers of the set C_2 .... then

$$\phi(m, r) = \sum_{n=0}^{m-1} f(m, n)\, \rho^{nr} = \prod_{i=1}^{\lambda} \left(\sum_{\alpha=1}^{q_i} \rho^{r\beta\alpha_i} \right)^{\alpha_i}.$$

By an argument similar to the one used in the previous theorem we have the result.

THEOREM 7.

$$C_i^r = \sum A_k C_k \text{ where}$$

$$A_k = \frac{\phi^r(m)}{m} \prod_{\substack{p|m \\ p \nmid t_k}} \left[\frac{(p-1)^r - (-1)^r}{(p-1)^r} \right] \prod_{p|t_k} \left[\frac{(p-1)^{r-1} - (-1)^{r-1}}{(p-1)^{r-1}} \right]$$

p *being a prime number,* $\phi^r(m) = [\phi(m)]^r$ *and* $\phi(m)$ *is Euler's totient function.*

Proof.—As before if $f(m, n)$ is the number of representations of n as the sum (mod m) of r integers of the set C_1 then we have easily

$$\sum_{n=0}^{m-1} f(m, n)\, \rho^{n\lambda} = C_m^r(\lambda)$$

and by the usual inversion (lemma C) we have

$$f(m, n) = \frac{1}{m} \sum_{\delta | m} C_m^r(\delta)\, C_{\frac{m}{\delta}}(n).$$

By lemma A we have

$$f(m, n) = \frac{\phi^r(m)}{m} \sum_{\delta | m} \frac{\mu^r(\delta)}{\phi^r(\delta)} C_\delta(n)$$

$$= \frac{\phi^r(m)}{m} \prod_{p | m} \left[1 + \frac{(-1)^r}{\phi^r(p)} C_p(n)\right]$$

But[5] $C_p(n) = -1$ if $p \nmid n$ and $= p - 1$ if $p | n$. Using this we have the required result.

Corollaries.—(1) *If* m *is even then every odd number is the sum* (*mod* m) *of* 3 *and every even number is the sum* (*mod* m) *of* 2 *numbers less than and prime to* m.

(2) *If* m *is odd then every number is the sum* (*mod* m) *of two numbers less than and prime to* m.

These follow easily from the above theorem because we have merely to find the least r for which no A_k is zero when m is even all A_k's, for which the corresponding t_k's are even, are zeroes. When m is odd, $r = 2$, no A_k is zero.

$$(3) \qquad \sum_{k=1}^{m} C_m^r(k) = \phi^r(m) \prod_{p | m} \left[1 - \frac{(-1)^{r-1}}{(p-1)^{r-1}}\right].$$

This follows easily from the result $\sum_{n=0}^{m-1} f(m, n)\, \rho^{n\lambda} = C_m^r(\lambda)$ by using lemma A and putting $n = m$.

$$(4) \qquad \sum_{k=1}^{m} C_m^2(k) = m\phi(m).$$

5. We shall study the problem similar to that considered by Von Sterneck but confining ourselves to the integers less than and prime to m.

THEORFM 8.—*If* f(m, n) *denotes the excess of the number of relative partions of* n (*mod* m) *into an even number of parts over those into an odd number, the parts being all distinct and chosen from the set of integers less than and prime to* m *then*

$$f(m, n) = \frac{1}{m} \sum \text{Exp.} \left(\frac{\wedge\left(\frac{m}{\delta}\right) \phi(m)}{\phi\left(\frac{m}{\delta}\right)} \right) C_{\frac{m}{\delta}}(n)$$

where Exp. (x) *means* e *and* $\wedge$ (n) *is the arithmetic function defined by*

$$-\frac{d}{ds} \log \zeta(s) = \sum_{n=1}^{\infty} \frac{\wedge(n)}{n^s}.$$

ζ (s) *being Riemann zeta function.*

Proof.—Using the notation of Section 3 we have

$$\left(1-\rho^{\beta_{11}r}\right)\left(1-\rho^{\beta_{21}r}\right)\ldots\left(1-\rho^{\beta_{\sigma_1 1}r}\right)=\sum_{k=0}^{m-1} f(m,k)\,\rho^{kr}.$$

But it is known[4] that

$$\left(1-\rho^{\beta_{11}}\right)\left(1-\rho^{\beta_{21}}\right)\ldots\left(1-\rho^{\beta_{\sigma_1 1}}\right)=e^{\Lambda(m)} \text{ and therefore}$$

$$\sum_{k=0}^{m-1} f(m,k)\,\rho^{kr}=\operatorname{Exp}\left[\frac{\Lambda\left(\frac{m}{d}\right)\phi(m)}{\phi\left(\frac{m}{d}\right)}\right]$$

using lemma C we have the required result.

6. It is well known[7] that if $\rho_1, \rho_2 \ldots \rho_\lambda$ $\lambda=\phi(m)$ be the primitive mth roots of unity then

$$(x-\rho_1)(x-\rho_2)\ldots(x-\rho_\lambda)=\prod_{d\mid m}\left(x^d-1\right)^{\mu\left(\frac{m}{d}\right)}.$$

It is known from Newton's theorem that the coefficients in the product could be expressed in terms of the sums of powers of roots. But

$$\rho_1^k+\rho_2^k+\ldots+\rho_\lambda^k=C_m(k)$$

and thus we get

$$\prod_{d\mid m}\left(x^d-1\right)^{\mu\left(\frac{m}{d}\right)}=\sum_{r=0}^{\lambda} A_r x^r \qquad \text{where}$$

$$A_r=\frac{(-1)^r}{r!}\begin{vmatrix} C_m(1) & 1 & 0 & \ldots & 0 \\ C_m(2) & C_m(1) & 2 & \ldots & 0 \\ \ldots & \ldots & \ldots & \ldots & \ldots \\ C_m(r-1) & C_m(r-2) & \ldots & C_m(1) & (r-1) \\ C_m(r) & C_m(r-1) & \ldots & C_m(1) & \end{vmatrix}$$

which shows that if m has a square factor (at least) prime to $r!$ A_r and all the previous ones therefore vanish. It is also of interest to notice that since

$$(1-\rho_1)(1-\rho_2)\ldots(1-\rho_\lambda)=e^{\Lambda(m)}$$

we have $$A_0+A_1+A_2+\ldots+A_\lambda=e^{\Lambda(m)}$$

which shows that a cyclotomic equation (Kreisteilungsgleichung) of degree $\phi(m)$ has the sum of the positive coefficients greater than the negative ones always. since $e^{\Lambda(m)}$ is never negative.

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[7] B. L. Van der Waerden, *Moderne Algebra*, Bd. 1, p. 108.

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